A STUDY ON

THERMAL CHARACTERISTICS OF POLYMER COMPOSITES FILLED WITH MICRO SIZED TiO_2 PARTICLES

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE

REQUIRMENTS FOR THE DEGREE OF

Master of Technology
(By Research**)**
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By

MADHUSMITA SAHU
Roll No. 611 ME 307

Under the supervision of

Dr. Alok Satapathy
Associate Professor
Department of Mechanical Engineering
National Institute of Technology
Rourkela

DEPARTMENT OF MECHANICAL ENGINEERING
National Institute of Technology
Rourkela, India
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In Loving Memory

of My Late Grand Mother

National Institute of Technology
Rourkela

C E R T I F I C A T E

This is to certify that the thesis entitled ***A Study on Thermal Characteristics of Polymer Composites Filled with Micro-sized TiO_2 Particles*** submitted by **MADHUSMITA SAHU** to National Institute of Technology, Rourkela for the award of the degree of **Master of Technology (By Research)** in *Mechanical Engineering* is an authentic record of research work carried out by her under my guidance and supervision.

The work incorporated in this thesis has not been, to the best of my knowledge, submitted to any other University or Institute for the award of a degree or diploma.

Dr. Alok Satapathy
Associate Professor
Department of Mechanical Engineering,
National Institute of Technology
Rourkela

A C K N O W L E D G E M E N T

Success can never be achieved alone. This thesis is a conscientious result of guidance of such people around me who have brought me all through the way. I am extremely fortunate to be involved in such a research work of this kind. It has enriched my life, giving me an opportunity to work in a new area of thermal behaviour of polymeric materials and showing me a direction for my future research.

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Place: Rourkela Madhusmita Sahu

Date: Roll No-611ME307

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Abstract

This thesis reports on the research dealing with the processing and characterization of TiO_2 filled polymer composites. The first part of the work includes the description of the materials used and the details of the experiments that are done during this research. It also presents the test results in regard to the physical, mechanical and micro-structural characteristics of the epoxy and polypropylene composites filled with micro-sized TiO_2 particles. The second part depicts the development of a theoretical heat conduction model based on which a mathematical correlation has been proposed for estimation of effective thermal conductivity of polymer composites with uniformly distributed micro-sized particulate fillers. In this part, the correlation is validated for TiO_2 filled polymers through numerical analysis and experimentation. The last part has reported on the epoxy and polypropylene composites in regard to their other thermal characteristics such as glass transition temperature (T_g) and coefficient of thermal expansion (CTE). The effects of TiO_2 content on these properties of epoxy and polypropylene have been studied experimentally. The estimation of effective thermal conductivity of the composites using finite element method (FEM) and using the proposed theoretical models is done and the results are validated by corresponding experimental results.

The findings of this research suggest that incorporation of TiO_2 into epoxy and polypropylene leads to substantial improvement in thermal conductivity and glass transition temperature of the resins. At the same time, TiO_2 helps in lowering the coefficient of thermal expansion of such composites. This work further shows that the FEM serves as a good predictive tool for assessment of thermal conductivity of these composites. The theoretical correlation proposed in this work can serve as a very good empirical model for spherical inclusions to estimate the effective thermal conductivity of the composites within the percolation limit.

With light weight and improved heat conduction capability, the TiO_2 filled polymer composites can be used for applications such as electronic packaging, encapsulations, communication devices, thermal interface material, printed circuit board substrates etc.

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CONTENTS

Chapter 1

INTRODUCTION

1.1 Background and Motivation

Requirement of Thermal Conduction

It is known that micro-electronic packaging plays an increasingly important role in the rapid progress of the electronic and electrical technologies. With the increase in integration scale of the microelectronic circuit, more and more heat is produced when the circuit works. The heat must be dissipated away in time to avoid over-heat occurrence, which requires that the packaging materials should have good thermal conductivity besides having traditional physico-mechanical properties. These packaging materials must possess low relative permittivity and low dielectric loss to reduce the signal propagation delay, which in turn provides better device performance. They should also have a low thermal expansion coefficient.

As the demands in denser and faster circuits intensify, the heat dissipation in microelectronic packaging is becoming increasingly important. Indeed, the inability to adequately conduct heat away from the chip has imposed another engineering constraint in many new product designs [1]. Traditionally, thermal problem in encapsulated devices has been addressed by the use of high cost embedded heat sinks, which are often susceptible to thermal cracking and of limited utility in thinner package configurations [2]. Polymers and ceramics have good electrical, mechanical and thermal properties and so there is a growing demand for them as packaging materials [3]. However, common polymers for packaging, such as epoxy, polyester, polyethylene (PE), polypropylene (PP), polyamide (PA), acrylonitrile-butadiene-styrene (ABS), and polyimide, etc. have low thermal conductivities. Because of this, they cannot effectively dissipate heat when used in various devices and their high thermal expansion (CTE) coefficients result in thermal failure.

Under this circumstance, emerged a class of promising packaging materials – *polymer composites*. Particulate filled polymer composites i.e. polymers filled with thermally conductive particulate matters are coming up as a cost effective way to cope with such thermal management issues [4].

Unfortunately, there is no widely accepted definition for a composite material. It can however be defined as any multiphase material that is artificially made and exhibits a significant proportion of the properties of the constituent phases. The constituent phases of a composite are usually of macro sized portions, differ in form and chemical composition and essentially insoluble in each other. The properties of composites are a function of the properties of the constituent phases, their relative amounts and size-and-shape of dispersed phase.

1.2 Composite Materials

Composites are combinations of two materials in which one of the materials, called the reinforcing phase, is in the form of fiber sheets or particles and are embedded in the other material called the matrix phase. The primary functions of the matrix are to transfer stresses between the reinforcing fibers/particles and to protect them from mechanical and/or environmental damage whereas the presence of fibers/particles in a composite improves its mechanical properties such as strength, stiffness etc. A composite is therefore a synergistic combination of two or more micro-constituents that differ in physical form and chemical composition and which are insoluble in each other. The objective is to take advantage of the superior properties of both materials without compromising on the weakness of either.

Composite materials have successfully substituted the traditional materials in several light weight and high strength applications. The reasons why composites are selected for such applications are mainly their high strength-to-weight ratio, high tensile strength at elevated temperatures, high creep resistance and high toughness. Typically, in a composite, the reinforcing materials are strong with

low densities while the matrix is usually a ductile or tough material. If the composite is designed and fabricated correctly, it combines the strength of the reinforcement with the toughness of the matrix to achieve a combination of desirable properties not available in any single conventional material. The strength of the composites depends primarily on the amount, arrangement and type of fiber and /or particle reinforcement in the resin.

The 'composites' concept is not a human invention. For example, wood is a natural composite material consisting of one species of polymer — cellulose fibers with good strength and stiffness — in a resinous matrix of another polymer, the polysaccharide lignin. Thus in composites, materials are combined in such a way as to enable us to make better use of their virtues while minimizing to some extent the effects of their deficiencies. This process of optimization can release a designer from the constraints associated with the selection and manufacture of conventional materials. He can make use of tougher and lighter materials, with properties that can be tailored to suit particular design requirements. And because of the ease with which complex shapes can be manufactured, the complete rethinking of an established design in terms of composites can often lead to both cheaper and better solutions.

A structural composite is a material that consists of two or more phases on a macroscopic scale, whose mechanical performance and properties are designed to be superior to those of the constituent materials acting independently. One of the phases is usually discontinuous, stiffer and stronger and is called the *reinforcement*, whereas the less stiff and weaker phase is continuous and is called the *matrix*. The properties of a composite material depend on the properties of the constituents, geometry and distribution of the phases. One of the most important parameters is the volume (or weight) fraction of reinforcement. The distribution of the reinforcement determines the homogeneity or uniformity of the material system. The more non-uniform is the reinforcement distribution, the more heterogeneous is the material and the higher is the probability of failure in the weakest areas. The geometry and orientation of the reinforcement affect the anisotropy of the system.

The phases of the composite system have different roles that depend on the type and application of the composite material. In the case of low to medium performance composite materials, the reinforcement, usually in the form of short fibers and particles, provides some stiffening but only local strengthening of the material. The matrix, on the other hand, is the main load-bearing constituent governing the mechanical properties of the material. In the case of high performance structural composites, the usually continous-fiber reinforcement is the backbone of the material that determines its stiffness and strength in the direction of fibers. The matrix phase provides protection and support for the sensitive fibers and local stress transfer from one fiber to another. The interphase although small in size, can play an important role in controlling the failure mechanisms and composite properties.

1.2.1 Types of Composite Materials

Broadly, composite materials can be classified into three groups on the basis of matrix material. They are:

a) Metal Matrix Composites (MMC)
b) Ceramic Matrix Composites (CMC)
c) Polymer Matrix Composites (PMC)

a) Metal Matrix Composites:

Metal Matrix Composites have many advantages over monolithic metals like higher specific modulus, higher specific strength, better properties at elevated temperatures and lower coefficient of thermal expansion. Because of these attributes metal matrix composites are under consideration for wide range of applications viz. combustion chamber nozzle (in rocket, space shuttle), housings, tubing, cables, heat exchangers, structural members etc.

b) Ceramic Matrix Composites:

One of the main objectives in producing ceramic matrix composites is to increase the toughness. Naturally it is hoped and indeed often found that there is a concomitant improvement in strength and stiffness of ceramic matrix composites.

c) Polymer Matrix Composites:

Most commonly used matrix materials are polymeric. The reasons for this are two-fold. In general the mechanical properties of polymers are inadequate for many structural purposes. In particular their strength and stiffness are low compared to metals and ceramics. These difficulties are overcome by reinforcing other materials with polymers. Secondly the processing of polymer matrix composites need not involve high pressure and does not require high temperature. Also equipments required for manufacturing polymer matrix composites are simpler. For this reason polymer composites developed rapidly and soon became popular for structural applications. These composites are used because overall properties of the composites are superior to those of the individual polymers. They have a greater elastic modulus than the neat polymer but are not as brittle as ceramics.

Broadly, polymer composites can be classified into two groups on the basis of reinforcing material: Fiber Reinforced Polymer (FRP) and Particle Reinforced Polymer (PRP). The classification is shown in Figure 1.1.

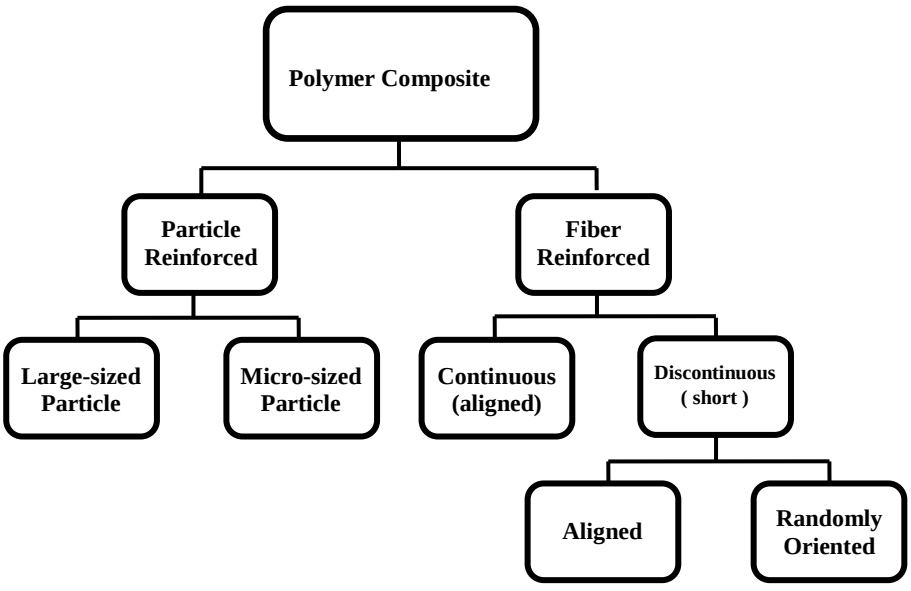

Figure 1.1 Classification of composites based on reinforcement type

Fiber reinforced polymer

Common fiber reinforced composites are composed of fibers and a matrix. Fibers are the reinforcement and the main source of strength while matrix glues all the fibers together in shape and transfers stresses between the reinforcing fibers. The fibers carry the loads along their longitudinal directions. Sometimes, filler might be added to smooth the manufacturing process, to impart special properties to the composites and/or to reduce the product cost. Common fiber reinforcing agents include asbestos, carbon/ graphite fibers, beryllium, beryllium carbide, beryllium oxide, molybdenum, aluminium oxide, glass fibers, polyamide, natural fibers etc. Similarly common matrix materials include epoxy, phenolic resin, polyester, polyurethane, vinyl ester etc. Among these resin materials, polyester is most widely used. Epoxy, which has higher adhesion and less shrinkage than polyesters, comes in second for its high cost.

Particle reinforced polymer

Particles used for reinforcing include ceramics, small mineral particles, metal powders such as aluminium and amorphous materials, including polymers and carbon black. Particles are used to increase the modulus and to decrease the ductility of the matrix. Particles are also used to reduce the cost of the composites. Reinforcements and matrices can be common, inexpensive materials and are easily processed. Some of the useful properties of ceramics and glasses include high melting temperature, low density, high strength, stiffness, wear resistance and corrosion resistance. Many ceramics are good electrical and thermal insulators. Some ceramics have special properties; some ceramics are magnetic materials; some are piezoelectric materials; and a few special ceramics are even superconductors at very low temperatures. However, ceramics have one major drawback: they are brittle. An example of particle – reinforced composites is an automobile tyre, which has carbon black particles in a matrix of poly-isobutylene elastomeric polymer.

1.2.2 Applications of Composites

This is a brief listing of current and proposed applications of composite materials in various branches of industry.

Aerospace

A wide range of load-bearing and non-load-bearing components are already in use in both fixed-wing and rotary wing aircraft. Many military and civil aircraft now contain substantial quantities of lightweight, high-strength carbon, kevlar and glass-fiber composites, as laminated panels and mouldings, and as composite honeycomb structures with metallic or resin-impregnated paper honeycomb core materials. They are used in air frames, wing spars, spoilers, tail-plane structures, fuel tanks, drop tanks, bulkheads, flooring, helicopter rotor blades, propellers and structural components, pressured gas containers, and landing gear doors, fairings, engine nacelles, air distribution ducts, seat components, access panels and so forth. Many modern light aircraft are being increasingly designed to contain as much light weight composite material as possible. For elevated-temperature applications, carbon-fiber reinforced materials are in use. Concord's disk brakes use this material, rocket nozzles and re-entry shields have been fashioned from it, and there are other possibilities for its use as static components in jet engines. Rocket motor casings and rocket launchers are also often made of reinforced plastics.

Automotive Engineering

There has been an increasing interest in weight reduction in order to permit both energy conservation and increased motoring economy. Reduction in the weight of an automobile structure achieves primary weight-saving and if carried to sufficiently great lengths enables the designer to use smaller power plants, thus achieving substantial secondary improvements in fuel economy. The majority of automotive applications involve glass-reinforced plastics (GRP) because the extra cost of carbon or aramid fiber is rarely considered to be acceptable in this market. Even so, the cost of using GRP is usually being weighed against the

much lower cost of pressed steel components, and the substitution is often rejected on purely economic grounds, leaving aside the question of energy saving. A wide range of car and truck body mouldings, panels and doors is currently in service, including complete front-end mouldings, fascias, bumper mouldings and various kinds of trim. There is considerable interest in the use of controlled crush components based on the high energy-absorbing qualities of materials like GRP. Leaf and coil springs, truck drive shafts and GRP wheel rims and inlet manifolds are also in service.

Bio-Engineering

Carbon-fiber reinforced plastic and carbon components are in use for prosthetic purposes, such as in orthopedic fracture fixation plates, femoral stems for hip replacements, mandibular and maxillary prostheses (jaw remodeling, for example), and for external orthotic supports in cases of limb deformity etc. Pyrolytic carbon is used to manufacture heart valve components and the substitution of a carbon/carbon composite is not unlikely. There have also been developments in the use of particulate hydroxyapatite as filler in a thermoplastic composite for bone remodeling or replacement.

Chemical Engineering

A substantial amount of polymer composites both fiber reinforced and particulate filled are currently in use in chemical plants for containers, pressure vessels, pipe-work, valves, centrifuges etc. These may be filament-wound or moulded components for containment of process fluids.

Domestic appliances

Injection-moulded reinforced thermoplastics and polyester moulding compounds are perhaps the most common composites used in consumer items for the domestic market, and the range is vast. Mouldings of all kinds, from kitchen equipment of all kinds to casings for the whole gamut of domestic and professional electrical equipment, motor-cycle crash helmets, television and computer casings and furniture.

Electrical Engineering

Typical applications are radomes, structural components for switch gear, power generator coolant containment and large-diameter butterfly valves, high-strength insulators (*eg.* for overhead conductor systems), printed circuit boards, and casings for electronic equipment. The use of composites which are more thermally stable and more moisture-resistant is increasingly predicated for sensitive, small-scale electronic components. Many prototype and practical wind-generator designs incorporate polymer composites or hybrid blading.

Marine Engineering

Marine applications include surface vessels, offshore structures and underwater applications. A vast range of pleasure craft has long been produced in GRP, but much serious use is also made of the same materials for hull and superstructure construction of passenger transport vessels, fishing boats and military vessels. Sea-water cooling circuits may also be made of GRP as well as hulls and other structures. Off-shore structures such as oil rigs also make use of polymer composites, especially if they can be shown to improve on the safety of steel structures, for fire protection piping circuits, walkways, flooring, ladders, tanks and storage vessels, blast panels, and accommodation modules. High specific compression properties also make composite materials attractive for submersibles and submarine structures, both for oil exploration and for military purposes.

Sports goods

Perhaps the most visible development in the use of composites, in recent time, has been in the sports goods industry. Manufacturers have been quick to seize on the potential advantages of new materials like carbon and boron fiber composites over conventional wood and metal for sports equipment of all kinds. Polymer composites are being increasingly used in tennis rackets, cricket bats, golf clubs, fishing rods, boats, oars, archery equipment, canoes and canoeing gear, surf

boards, wind-surfers, skateboards, skis, ski-poles, bicycles and protective equipment of one kind or another.

The technology of composite materials has thus experienced a rapid development in last two decades due to (a) significant progress in materials science and technology in the area of fibers, polymers and ceramics (b) requirements for high performance materials in aircraft and aerospace structures (c) development of powerful and sophisticated analysis using modern numerical methods for structural analysis using modern computer technology. Prospects for the future are bright as cost is decreasing due to market expansion, fabrication process is becoming less costly and automation is introduced. But in spite of all these rapid developments, the fact remains that compared to fiber reinforced polymers, research on the particulate filled polymer composites has drawn much less attention of the scientific community. In view of this, the present work is undertaken to study certain aspects of a class of particulate-polymer composites.

1.3 Introduction to the Research Topic

The present piece of research is basically an experimental investigation focused on the thermal characteristics of a new class of particulate filled polymer composites. It also includes fabrication of the composites and their physical and mechanical characterization.

Miniaturization of electronic devices due to their less space need and higher portability is the demand of the customer of recent times. Applications in electronic industry therefore are requiring superior materials for packaging and encapsulation. They should also have good properties such as high thermal conductivity to dissipate the heat generated and low thermal expansion coefficient to match with that of silicon. Basic electronic components may be packaged discretely, as arrays or networks of like components or integrated inside packages such as semiconductor integrated circuits, hybrid integrated circuits, or thick film devices. A modern packaging application therefore

embodies a host of materials and necessitates an integrated design approach from the very outset.

Last few decades have seen a rapid advancement in electronics technology as there is a constant demand for miniaturization and hence the sizes are gradually shrinking whereas the number of components and communication speed are increasing day-by-day which leads to a generation of high amount of heat and gives rise to problems in heat dissipation. Neat polymers like epoxy or polyester are commonly used as material for heat sink applications but they suffer from a drawback of low thermal conductivity. If these polymers are filled with metal powders like aluminum and copper, the thermal conductivity improves. But at the same time their electrical resistivity drops and there is possibility of a rise in their effective dielectric constants. For this reason, ceramics are preferred over metal powders as fillers in polymeric matrices.

Thermal conductivity is an important parameter for characterization of thermal properties of inorganic particulate-filled polymer composites. Various complicated factors affect the thermal conductivity of such materials. In view of this, a theoretical heat transfer model for estimation of effective thermal conductivity of filled polymer is developed based on the law of minimal thermal resistance and equal law of specific equivalent thermal conductivity. Effects of particulate fillers on other thermal characteristics such as glass transition temperature and coefficient of thermal expansion of the composites are also studied.

Thermoset epoxy and thermoplastic polypropylene are chosen as the polymers to be used as the matrix materials for this work. For more than 30 years, epoxy and polypropylene have played a critical role in electronic assemblies. They were first introduced into the hybrid industry and enjoyed much success in bonding components, protecting devices and hermetically sealing packages. Just as they provided an attractive alternative to eutectic bonding in hybrids, they were implemented in semiconductor packaging. Today, nearly 80% of the world die

attach market for plastic encapsulated devices is solvent-less conductive epoxies. A few reasons why epoxies are wide spread and commonplace in electronic assemblies include: low temperature cure profiles allow for greater availability of substrates and temperature sensitive components; compliant nature of the polymer; low out-gassing and good thermal stability at elevated temperatures; very good chemical and solvent resistance; 100% solid systems are environmentally benign; and epoxies readily accept fillers. Polypropylene also has similar characteristics that are desirable for such applications.

Micro-sized titanium dioxide (TiO_2) is taken as the filler material in the epoxy and polypropylene resins in the present investigation. TiO_2 with a moderate thermal conductivity and low CTE is a potential filler material to be used in polymeric matrices. The objective of this work is to analyze the heat transport through these epoxy-TiO_2 and polypropylene-TiO_2 composites and to evaluate the effective thermal conductivities of these composites by numerical, analytical as well as experimental methods. Through addition of highly conductive inorganic filler into the resin matrix, it is possible to achieve a better thermal conduction path and decrease the thermal contact resistance at the filler–resin matrix interface that attributes to increase in thermal conductivity.

1.4 Thesis Outline

The remainder of this thesis is organized as follows:

Chapter 2: Includes a literature review designed to provide a summary of the base of knowledge already available involving the issues of interest. It presents the research works of previous investigators on particulate reinforced polymer composites with emphasis on their thermal behavior.

Chapter 3: Includes a description of the raw materials and the test procedures. It presents the details of fabrication and characterization of the composites under investigation.

Chapter 4: Presents the test results in regard to the physical, mechanical and micro-structural characteristics of the composites under study.

Chapter 5: Presents the development of a theoretical model for estimation of effective thermal conductivity of particulate filled polymer composites. This model is validated through numerical and experimental investigation for a set of epoxy-TiO_2 composites.

Chapter 6: Presents the theoretical and experimental results for effective thermal conductivity of a set of polypropylene-TiO_2 composites. It also provides the effects of TiO_2 addition on glass transition temperature and coefficient of thermal expansion of polypropylene.

Chapter 7: Provides a summary of the findings of this research work, outlines specific conclusions drawn from both the experimental and analytical efforts and suggests ideas and directions for future research.

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Chapter 2

LITERATURE REVIEW

In the current chapter, the summary of the literature surveyed during the research has been presented. The purpose of this literature survey is to provide background information on the issues related to the present investigation and thereby to outline the objectives. This treatise thus embraces various aspects of particulate filled polymer composites with a special reference to their thermal characteristics. It includes reviews of available research reports:

- On particulate filled polymer matrix composites
- On thermal conductivity of particulate filled polymers
- On thermal conductivity models
- On T_g and CTE of polymer composites
- On TiO_2 filled polymer matrix composites

At the end of the chapter a summary of the literature survey and the knowledge gap in earlier investigations are presented. Subsequently the objectives of the present research work are also outlined.

2.1. On Particulate Filled Polymer Matrix Composites

Polymers and polymer matrix composites are widely acceptable in several industries. These polymer matrix composites are basically consisting of polymers with added filler according to amendment required in the polymer used. These fillers are added to the polymers to improve the cost reduction, improved processing, density control, optical effects, thermal conductivity, control of thermal expansion, electrical properties, magnetic properties, flame retardancy and improved mechanical properties such as hardness and wear resistance. Hard particulate fillers consisting of ceramic or metal particles and fiber fillers made of glass are being used these days to dramatically improve the

wear resistance even up to three orders of magnitude [5]. Various kinds of polymers and polymer matrix composites reinforced with metal particles have a wide range of industrial applications such as heaters, electrodes [6], composites with thermal durability at high temperatures [7] etc. These engineering composites are desired due to their low density, high corrosion resistance, ease of fabrication and low cost [8-10]. Similarly, ceramic filled polymer composites have been the subject of extensive research in last two decades. The inclusion of inorganic fillers into polymers for commercial applications is primarily aimed at the cost reduction and stiffness improvement [11,12]. Along with fiber-reinforced composites, the composites made with particulate fillers have been found to perform well in many real operational conditions. It is reported by Bonner [13] that with the inclusion of micro-sized particulates into polymers, a high filler content (typically greater than 20 vol%) is generally required to bring the above stated positive effects into play. But at the same time, as already mentioned, this may also have detrimental effects on some important properties of the matrix polymers such as processability, appearance, density and aging performance.

When silica particles are added into a polymer matrix to form a composite, they play an important role in improving electrical, mechanical and thermal properties of the composites [14, 15]. Recently, reduction in particle size is being adopted by various researchers and many studies have focused on how single particle size affects mechanical properties of the composites [16–22]. The shape, size, volume fraction and specific surface area of such added particles have been found to affect mechanical properties of the composites greatly. Yamamoto et al. [23] reported that the structure and shape of silica particles have significant effects on the mechanical properties such as fatigue resistance, tensile and fracture properties. Nakamura et al. [24–26] discussed the effects of size and shape of silica particles on the strength and fracture toughness based on particle-matrix adhesion and also found an increase in the flexural and tensile strength as specific surface area of particles increased. Moloney et al. [27–29]

and Adachi et al. [30] found that the mechanical properties of epoxy composites were dependent on volume fraction of particles. Furthermore, effects of different particles of micron size magnitude and nano-particles on the properties of the composites were discussed by Yuan et al. [31] and Ng et al. [32].

Formulation and production of particulate composites is mostly based on two main principles, a filler theory and a mastic (filler matrix system) theory. As per the filler theory [33, 34], optimal composite properties are achieved when the particle size distribution permits a maximal packing of the filler particles and according to the mastic theory [33, 34], the matrix creates a coating on each filler particle with an optimal thickness. This provides a contact between the filler particles producing a rigid and stable composite mixture. Concerning these theories, two main parameters - the particle size distribution of the filler and the optimal matrix content for this distribution influence the behavior of the composite. Other parameters affecting the mechanical behavior of these composites are wetting of the filler by the resin and the adhesion between the two components. Physico-chemical parameters of the filler which affect the initial behaviour and durability of the composite mixture include shape, surface activity and area, size and size distribution. Detailed discussions on these parameters have been reported by Karger and Stokes et al. [35, 36]. Srivastava and Shembekar [37] studied the fracture toughness of epoxy resin and it is observed that there is an improvement in toughness by addition of fly ash particles as filler. The fillers also affect the tensile properties according to their packing characteristics, size and interfacial bonding. The maximum volumetric packing fraction of filler reflects the size distribution and shape of the particles [38]. Inorganic nanoparticles such as silicon dioxide (SiO_2) [39–42], titanium dioxide (TiO_2) [43–46], aluminium oxide (Al_2O_3) [47,48] and zinc dioxide (ZrO_2) [49,50] have been used in the past to improve polymer properties. Sulong et.al. [51] investigated the rheological properties of highly filled metal powder (SS316L) in a polymer matrix composite combined with carbon nanotubes (CNTs) and graphite. Das et.al. [52] studied structural, thermal, mechanical and

dynamic mechanical properties of cenosphere filled polypropylene and found that damping properties, tensile modulus enhanced and tensile strength and impact strength decreased with increase in filler content. Liang et.al. [53] have recently reported on the reinforcement and quantitative description of inorganic particulate-filled polymer composites and concluded several reinforcing theories on the basis of the previous studies. Theories such as interfacial adhesion reinforcing theory, filler inducing crystallization reinforcing theory, filler frame reinforcing theory, and synergistic reinforcing effect theory suggest that reinforcing effects should be related closely to the filler shape and size, in addition to the filler concentration and dispersion in the matrix.

2.2. On Thermal Conductivity of Polymer Matrix Composites

Considerable work has been reported in available literature on the heat transport in polymers by Hennig and Knappe [54], Hansen and Ho [55], Peng and Landel [56], Choy and Young [57] etc. Later on, Tavman [58] successfully provided a criterion for anisotropic heat conduction behaviour of polymers by changing their molecular orientation. In a recent work Griesinger et al. [59] have reported that the thermal conductivity of polyethylene increases from 0.35 to 50 W/m-K by keeping an orientation ratio of 50. However, most of these studies were confined to the thermal behaviour of neat polymers and not to their composites.

Since it is not always possible to fabricate a composite keeping the molecular orientation as per choice, a more practical method to increase the thermal conductivity of the polymer is by adding thermally conductive particles or fibers onto it. Lot of work has been reported to improve the thermal conductivity of polymers by incorporating conductive fillers. Most of them include experimental determination of effective thermal conductivity of particulate filled polymer composites [60-64].

Metals are known for their high thermal conductivity, so they are being widely used as fillers in polymer composites. Sofian et al. [60] studied the effect of

various metal powders like copper, zinc, iron and bronze on the thermal properties like conductivity, diffusivity and specific heat of high-density polyethylene matrix. Mamunya et al. [61] later reported the improvement in thermal conductivity of two different categories of polymers i.e. thermoplastic (polyvinyl chloride) and thermoset (epoxy) filled with copper and nickel particles. Though in 1990s, Tecke et al. [62] and Tavman [10] had already used copper powder as filler and measured the thermal conductivity of the composites by hot disk method, more recently copper has again been used by Luyt et al. [63] in low density polyethylene. They have reported around 150% increase in the value of thermal conductivity for the composites filled with 24 vol% of copper. Subsequently, Tavman [64] took aluminium powders as filler and studied the thermal property of high density polyethylene whereas later Boudenne et al. [65] gave an overview on the thermal conductivity of polypropylene/aluminium composites. Silver too has a high potential to be used as filler because of its high thermal conductivity. The effect of silver particulates in epoxy was studied by Bjorneklett et al. [66]. Although filling of a polymer with metallic particles resulted in increased thermal conductivity; simultaneous increase in density of the composites was also recorded, thus restricting the use of metal powders for light-weight applications.

Carbon-based fillers with high thermal conductivity and low density appear to be the most promising fillers for improving thermal conductivities of polymer composite. Graphite, carbon fiber and carbon black are well-known carbon-based fillers. Graphite is considered as the best conductive filler because of its good thermal conductivity and low cost [67]. Graphite with single graphene sheet shows intrinsically high thermal conductivity of about 800W/m-K [68]. Expanded graphite, an exfoliated form of graphite with layers of 20-100nm thickness, has also been used in polymer composites [69]. It was found that thermal conductivity of the chemically functionalized graphite/epoxy composite with such exfoliated graphite (20wt %) increased from 0.2 to 5.8 W/m-K. Carbon fiber, typically vapor grown carbon fiber (VGCF), is an important

carbon-based filler [70]. Studies conducted on modified thermal conductivity of polymer composites filled with carbon nanotubes have recently been reviewed by Han and Fina [71]. Metallic and carbon-based fillers are highly conductive thermally, but they are highly electrically conductive as well. There are certain areas where high thermal conductivity is required but at the same time electrical resistivity is of prime importance, like in electronic devices. In that case a balance is required that maximizes the thermal dissipation effect of the electrically insulating molding compound as well as which prevents the leakage of current across the conductors due to very low resistivity.

Ceramic powder reinforced polymer materials are being used extensively for micro- electronic applications because of their high thermal and low electrical conductivity. Some promising ceramic fillers such as SiC [72], Si_3N_4 [73], $Sr_2Ce_2Ti_5O_{16}$ [74], CeO_2 [75] AlN [76, 77], Al_2O_3 [78, 79] and ZnO [80] are in use to improve thermal conductivity of various polymers. It is observed from the above literature on ceramic particle filled polymers that there is an appreciable increase in thermal conductivity of the composite with increase in filler concentration whereas no significant changes are observed in electrical conductivity of such composites. Incorporation of multiple fillers into the polymer matrix for the improvement of thermal conductivity has also been reported [81- 83]. Factors other than the intrinsic thermal conductivity of the fillers such as shape, size, distribution and interconnectivity between the particles also decide the composite thermal conductivity. Boudenne et al. [65] studied the effect of two different particle sizes of aluminium filler and found that the composite filled with larger particle size shows significantly high thermal conductivity. It is due to the formation of more stable thermally conductive pathways in the matrix material. Similar behaviour was observed by Zhou et al. [84]. On the contrary, some authors have highlighted the higher heat transport ability of the composites filled with smaller particles [60,85]. Boudenne et al. [86] too experimented with copper powders instead of aluminum and found better thermal conductivity with particles of smaller size.

Weidenfeller et al. [87] studied the effect of the interconnectivity of the filler particles and its important role in improving the thermal conductivity of the composites. Tekce et al. [62] noticed the strong influence of the shape factor of fillers on thermal conductivity of the composite. Effects of interfacial thermal barrier resistance together with particle shape and size on the thermal conductivity was shown by Jiajun et al. [88]. Zhidong et al. [89] reviewed the status of worldwide research in thermal conductivity of CNTs and their polymer nanocomposites and observed that thermally conductive polymer based composites are tentatively prepared by incorporation of thermally conductive fillers. Chu et al.[90] investigated on the thermal conductivity of Cu-Zr/diamond composites and the thermal conductivity measurements showed that the thermal conductivity of composites varies somewhat up and down with the Zr added level, showing a maximum thermal conductivity value of 615W/mK at 1.2 wt% Zr content. Devendra et al.[91] investigated on thermal properties of E-glass filled epoxy composites by different filler materials like Al_2O_3, magnesium hydroxide, silicon carbide and hematite powder and observed that composites filled with 10 vol% of Al_2O_3 and Mg $(OH)_2$ exhibited low thermal conductivities. On the other hand 10 vol% of SiC exhibited high thermal conductivities i.e 3.515 W/m ˚C. Liang.[92] estimated thermal conductivity of polypropylene/hollow glass bead (HGB) composites and results showed that the predictions of the thermal conductivity were in good agreement with the measured data except to individual data points. Furthermore, both the estimated and measured thermal conductivity decreased roughly linearly with increasing the HGB volume fraction when the HGB volume fraction was less than 20%; the influence of the particle diameter on the thermal conductivity was insignificant.

Along with experimental investigation, few works has been reported using numerical methods for calculating effective thermal conductivity of composite materials [93,94]. A numerical approach to predict the conductivity of granular or fibrous reinforced composite materials was proposed by Veyret et al. [93],

whereas Kumlutas and Tavman [94] developed a numerical model up to 10 vol% of filler content which showed good agreement with the experimental values. Recently Nayak et al. [95] have estimated the effective thermal conductivity of pine wood dust filled epoxy composite by using finite element method. Ramani et.al. [96] established an automated finite element analysis method to determine the effective thermal conductivities of the composites. Yin and Tu [97] and Tu et. al. [98] developed 2-dimensional and 3-dimensional finite element models for PTFE composites with randomly distributed circular graphite particles. The model predicts that there is an inclusion to matrix saturation conductivity ratio at a certain volume fraction. Cai et.al. [99] studied the thermal conductivity of PTFE composites using a 3-dimensional finite element model, taking into account the size distribution of fillers. Zeng et.al. [100] also developed a finite element method to predict the effective thermal conductivity of particle filled epoxy composites.

2.3. On Thermal Conductivity Models

Several theoretical models and correlation have been established by various researchers to predict the effective thermal conductivity of two phase mixtures and composites. The Maxwell-Garnett model or M-G model (Maxwell, 1873) is the first theoretical model used to describe the effective thermal conductivity of two component mixtures. Comprehensive review articles have discussed the applicability of many of these models [101, 102]. For a two-component composite, the simplest alternatives would be with the materials arranged in either parallel or series with respect to heat flow, which gives the upper or lower bounds of effective thermal conductivity.

For the parallel conduction model:

$$k_c = (1-\phi)k_m + \phi k_f \qquad (2.1)$$

Where k_c, k_m, k_f are the thermal conductivities of the composite, the matrix and the filler respectively and ϕ is the volume fraction of filler.

For the series conduction model:

$$\frac{1}{k_c} = \frac{(1-\phi)}{k_m} + \frac{\phi}{k_f} \tag{2.2}$$

The above two correlations (2.1, 2.2) are derived on the basis of the Rule of Mixture (ROM). Taso [103] derived an equation relating the thermal conductivity of a two phase solid mixture to the conductivity of the individual components and to two parameters which describe the spatial distribution of the two phases. By assuming a parabolic distribution of the discontinuous phase in the continuous phase, Cheng and Vachon [104] obtained a solution to Tsao's model that did not require knowledge of additional parameters. Agari and Uno [105] propose a new model for polymers which takes into account parallel and series conduction mechanisms. According to this model, the expression that governs the thermal conductivity of the composite is:

$$\log k_c = \phi C_2 \log k_f + (1-\phi)\log(C_1 k_m) \tag{2.3}$$

Where, C_1, C_2 are experimentally determined constants of order unity. C_1 is a measure of the effect of the particles on the secondary structure of polymer, like crystallinity and the crystal size of the polymer. C_2 is the conductive chain formation potentiality of the particles. Bruggeman [106] derived an equation employing different assumptions for permeability and field strength for dilute suspension of spheres for a homogeneous medium and the implicit equation is given as:

$$1-\phi = \left[\frac{k_c - k_f}{k_m - k_f}\right]\left(\frac{k_m}{k_c}\right)^{1/3} \tag{2.4}$$

Kanari model [107] which is a revised Bruggmen's equation is another empirical model using inorganic particles as filler. It presents a relationship between the

thermal conductivity of composites and the volume fractions of filler which depends on the shape of the filler.

$$1-V_f = \frac{k_c - k_f}{k_m - k_f}\left(\frac{k_m}{k_c}\right)^{\frac{1}{(1+x)}} \tag{2.5}$$

Where V_f is the volume fraction of filler, k_c is the thermal conductivity of composite; k_f is the thermal conductivity of the filler; k_m is the thermal conductivity of the matrix; and x is the constant determined by sphericity of the filler and k_f/k_m, or only by the sphericity of the filler.

Lewis and Nielsen [108] derived a semi-theoretical model by modification of the Halpin-Tsai equation for a two phase system which assumes an isotropic particulate reinforcement and also takes into consideration the shape of particle as well as its orientation.

$$k_c = k_m\left[\frac{1+AB\phi}{1-B\phi\psi}\right] \tag{2.6}$$

Where $B = \left[\frac{(k_f/k_m)-1}{(k_f/k_m)+A}\right] and, \psi = 1+\left[\frac{1-\phi_m}{\phi_m^2}\right]$

where, k_f is thermal conductivity of filler material and 'ϕ' is the volume fraction of filler material. The value of A and ϕ_m for different shapes are provided in the Table 2.1 and 2.2 respectively.

Table 2.1 Value of A for various systems

Type of dispersed phase	Direction of heat flow	A
Cubes	Any	2
Spheres	Any	1.5
Aggregates of spheres	Any	$(2.5/\phi_m) -1$
Randomly oriented rods Aspect ratio=2	Any	1.58
Randomly oriented rods Aspect ratio=4	Any	2.08
Randomly oriented rods Aspect ratio=6	Any	2.8
Randomly oriented rods Aspect ratio=10	Any	4.93
Randomly oriented rods Aspect ratio=15	Any	8.38
Uniaxially oriented fibers	Parallel to fibers	2L/D
Uniaxially oriented fibers	Perpendicular to fibers	0.5

Table 2.2 Value of ϕ_m for various systems

Shape of particle	Type of packing	ϕ_m
Spheres	Hexagonal close	0.7405
Spheres	Face centred cubic	0.7405
Spheres	Body centred cubic	0.60
Spheres	Simple cubic	0.524
Spheres	Random close	0.637
Rods and fibres	Uniaxial hexagonal close	0.907
Rods and fibres	Uniaxial simple cubic	0.785
Rods and fibres	Uniaxial random	0.82
Rods and fibres	Three dimensional random	0.52

2.4. On T_g and CTE of Polymer Composites

Glass transition temperature and coefficient of thermal expansion play an important role in characterizing the thermal properties of polymer composites. Few works has been reported to resolve the problem of high CTE of polymers. Benito et al.[109] reported on CTE of TiO_2 filled EVA based nanocomposites and the influence of filler size on composites. Iyer et al. [110] have recently reported significant reduction in CTE as the content of BN is increased in the composite. Dey et al. [111] have studied the dependence of CTE on filler content at ambient temperature and Yasmin et. al. [112] have reported that, as the graphite concentration in epoxy increases, T_g increases and CTE decreases. Thomas et al. [113] studied about the effect of $Sm_2Si_2O_7$ particles as reinforcement in two different matrix materials (polyethylene and polystyrene) on CTE.

Li sun et.al.[114] reported addition of small amount of Al_2O_3 into the WO_3 + ZrO_2 reaction system was found to effectively increase the final densities and Young's moduli of the sintered composites and also shows remarkable change in CTE of these composites. Devendra et.al. [91] reported that with increase in the addition of filler materials to polymers, the thermal expansion coefficient of composites reduced. Dey et al. [111] investigated the thermal properties of silicon powder filled high-density polyethylene composites and reported that coefficient of thermal expansion of the composites showed strong dependence on silicon loading. Silica is used as the filler to reduce the CTE of under fill so as to match the CTE of the solder material to achieve high reliability [115]. Goyel et. al. [116] developed high performance polymer/AlN composites for electronic substrate application and found that it has unique combination of anisotropic linear coefficient of thermal expansion (CTE) and dielectric properties. Recently, Agrawal et.al. [117] have also reported on modified glass transition temperature and coefficient of thermal expansion (CTE) of epoxy

composites filled with AlN and Al_2O_3. Similar findings have also been reported by Mishra et.al. [118] for epoxy based composites filled with solid glass microspheres.

2.5. On TiO_2 Filled Polymer Matrix Composites

Polymers and their composites have great potential as packaging materials in electronic industries, but they are still the secondary choice for such applications as packaging and encapsulations mainly because of their very low thermal conductivity. Various fillers with high thermal conductivity can resolve the problem. Ceramics such as AlN, Al_2O_3, BN, BeO etc possess fairly good thermal conductivity and research has already been conducted on their use as conductive fillers. TiO_2 also happens to be a potential candidate for this purpose and there is a need to explore this possibility. It has a moderate thermal conductivity, high electrical resistivity and also a very low thermal expansion coefficient. Various researchers have studied several aspects of TiO_2 filled polymer composites in the past although studies on its thermal behaviour have not received adequate research attention so far.

Ikram et.al. [119] investigated the effect of addition of TiO_2 micro and nano sized particle on mechanical properties of TiO_2/epoxy composites and found that flexural strength and fracture toughness of epoxy-micro composites decreases with increasing the volume fraction of TiO_2 micro particles specially at high volume fraction while Youngs modulus increases with increasing volume fraction. Kontos et al [120] studied the electrical relaxation dynamics in TiO_2 filled polymer matrix composites in the frequency range of 0.1 Hz-1MHz and temperature from -100 to 150˚C. It has been observed that from lower to higher frequencies at constant temperature , the composites are attributed to interfacial polarization phenomena, glass transition and to relaxing polarization of the TiO_2 ceramic particles respectively. Tao et. al [121] studied about the high refractive index property of TiO_2 and observed that with 30 wt% loading of TiO_2 nanoparticles, the refractive index of epoxy improves to 1.62. Siriratet.al [122]

studied the effects of mixing conditions and particle sizes on mechanical and morphological properties of polypropylene composites. Jyotish kumar et.al [123] reported on preparation and properties of TiO_2 filled poly/epoxy hybrid composites and found that addition of TiO_2 induces a significant increase in tensile properties, impact strength and fracture toughness with respect to neat blend matrix. Polizos et.al.[124] investigated on the effects of synthesized titanium dioxide nanoparticles and found that uniform and small sized TiO_2 fillers (~10nm) dominated the electrical, dielectric and mechanical properties of the filled epoxy resin composites. Siddhartha et.al [125] reported on mechanical and dry sliding wear characterization of epoxy-TiO_2 particulate filled functionally graded composites materials and found that 20wt% epoxy-TiO_2 composites exhibit lowest specific wear rate and for flexural strength at a range of 5% increased for 20 wt% filler content and for tensile modulus 6% increase for 20 wt%, also impact strength increases by 92% for 20 wt% of TiO_2 content. Satapathy et.al. [126] have also reported on successful implementation of neural computation in analyzing the dry sliding wear behaviour of TiO_2–polyester composites. Several other investigators [127, 128, 129] used TiO_2 as a filler to modify the dielectric properties of the polymer composite. Wazzan et al. [130] reported that the toughness and impact resistance of DGEBA epoxy increased by 60%–65% in the presence of 4 wt% of titanium dioxide.

2.6 Knowledge Gap in Earlier Investigations

In spite of a number of research works reported in the past, there is a huge knowledge gap that demands a well-planned and systematic research in this area of particulate filled polymer composites. An exhaustive review of the published literature reveals that:

- Most of the investigations are aimed at enhancing the thermal conductivity of the polymer by adding metal powders, but only a few works include metal oxides as filler.

- The studies reported on thermal characteristics of particulate filled polymers have mostly been experimental and there are only a few reports on development of theoretical models.

- TiO_2 has previously been used in polymer composites by many investigators mostly for the purpose of modifying tensile, flexural and/or dielectric strength of the matrix polymer. But its use for enhancing thermal conductivity of epoxy and polypropylene has not so far been reported.

In view of the above, the present work is undertaken to investigate on the thermal characteristics such as effective thermal conductivity, glass transition temperature, coefficient of thermal expansion etc. of epoxy and polypropylene matrix composites filled with micro-sized TiO_2 particles**.** TiO_2 is chosen as the filler material due to its moderate thermal conductivity (about 11.7 W/m-K), high electrical resistivity, no toxicity and a low thermal expansion coefficient (8.6×10^{-6}/K).

2.7 Objectives of the Present Work

The objectives of this work are outlined as follows:

- Development of a theoretical model for estimation of effective thermal conductivity (k_{eff}) of polymer composites with micro-sized particulate fillers.
- Estimation of k_{eff} of particulate filled polymer composites using finite element method (FEM).
- Fabrication of different sets of epoxy and polypropylene composites filled with micro-sized TiO_2 particles and measurement of their thermal conductivities.
- Validation of proposed theoretical model and FEM results by comparing the theoretical values with the measured values of k_{eff} of the composites.
- Physical, mechanical and micro-structural characterization of the composites.

- Study of the effects of incorporating micro-sized TiO_2 particles on other thermal properties like glass transition temperature (T_g) and coefficient of thermal expansion (CTE) of epoxy and polypropylene and exploring the possibility of using them in micro-electronics applications.

Chapter Summary

This chapter has provided

- An exhaustive review of research works on various aspects of particulate filled polymer composites reported by previous investigators
- The knowledge gap in earlier investigations
- The objectives of the present work

The next chapter presents the materials used for fabricating various composites under this study and the details of various characterization tests carried out on them.

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Chapter 3

MATERIALS AND EXPERIMENTAL DETAILS

This chapter describes the materials and methods used for processing and characterizing the composites under investigation. It presents the details of the tests related to the physical, mechanical, micro-structural and thermal characterization of the epoxy and polypropylene composites prepared for this investigation.

3.1. MATERIALS

3.1.1. Matrix Material

Matrix materials used for processing of composites are of different types like metals, ceramics and polymers. Polymer are most commonly used as matrix material because of cost effectiveness, ease of fabricating complex parts with less tooling cost and they also have excellent room temperature properties when compared to metals and ceramic matrices. Polymer matrices can either be thermoplastic or thermoset in nature. Thermoset matrices are formed due to an irreversible chemical transformation of the resin into an amorphous cross-linked polymer matrix. Due to huge molecular structures, thermoset resins provide good electrical and thermal insulation. They have low viscosity, which allows proper fiber wet out, excellent thermal stability and better creep resistance [131].The most commonly used thermosets are epoxy, polyester, vinyl ester and phenolic resin.

Thermoplastic polymers are associated through chain due to intermolecular forces and these forces permits thermoplastics to be remolded because the intermolecular interactions increase upon cooling and restore the bulk properties. These sets of polymers are normally produced in one step and then are made into products in a subsequent process. Thermoplastic polymers can also be readily

recycled because each time they are reheated, they can again be reshaped or formed into a new article. Due to the reusability, these sets of polymers are widely accepted in industrial applications. Various types of thermoplastic polymers available in the market are acrylic, nylon, polyethylene, polypropylene, polystyrene, polyvinyl chloride, teflon.

3.1.1.1. Matrix Material-1(Epoxy)

Among the wide variety of thermosetting polymers available in the market, epoxy resins are widely being used for many advanced composites due to their excellent adhesion to a wide variety of fibers, superior mechanical and electrical properties and good performance at elevated temperatures. In addition to that they have low shrinkage upon curing and good chemical resistance. Due to several advantages over other thermoset polymers as mentioned above, epoxy (LY 556) is chosen as the matrix material for the present research work. It chemically belongs to the 'epoxide' family and its common name is Bisphenol-A-Diglycidyl-Ether (commonly abbreviated to DGEBA or BADGE).Its molecular chain structure is shown in Figure 3.1. It provides a solvent free room temperature curing system when it is combined with the hardener tri-ethylene-tetramine (TETA) which is an aliphatic primary amine with commercial designation HY 951 (Figure 3.2). The LY 556 epoxy resin (Figure 3.3) and the corresponding hardener HY-951 are procured from Ciba Geigy India Ltd. Table 3.1 provides some of the important properties of epoxy.

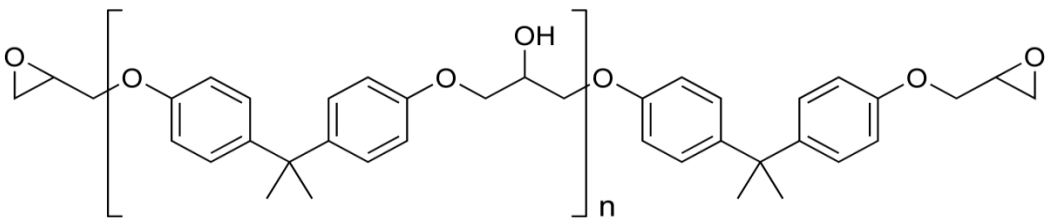

Figure 3.1 Unmodified epoxy resin chain ('**n**' denotes number of polymerized unit)

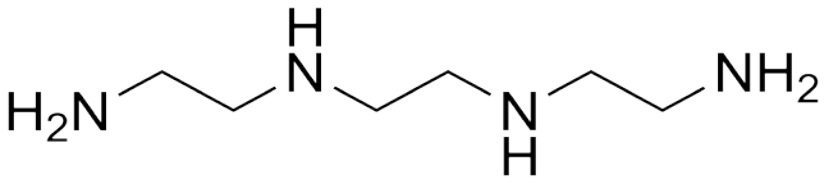

Figure 3.2 Tri-ethylene-tetramine (hardener used for epoxy matrix)

Table 3.1 Properties of epoxy resin

Characteristic Property	Inferences
Density	1.1 gm/cc
Compressive strength	90 MPa
Tensile strength	58 MPa
Micro-hardness	0.085 GPa
Thermal conductivity	0.363 W/m-K
Glass transition temperature	98°C
Coefficient of Thermal expansion	62.83 ppm /°C
Electrical conductivity	0.105×10^{-16} S/cm

Figure 3.3 Epoxy resin and hardener

3.1.1.2.Matrix Material-2 (Polypropylene)

Polypropylene also known as propene is another polymer used as the thermoplastic matrix for the present investigation. Molecular formula for polypropylene is $(C_3H_6)_n$, where n is the number of polymerized unit.Its molecular chain structure is shown in Figure 3.4.Polypropylene of homo-polymer M110 grade is chosen for the present research shown in Figure 3.5 are procured from CIPET, Bhubaneswar. Polypropylene is used for its good mechanical performance, aesthetics, resistance to chemicals, cost effectiveness and stability to heat and recyclability. Table 3.2 provides some important properties of polypropyleneused in this investigation.

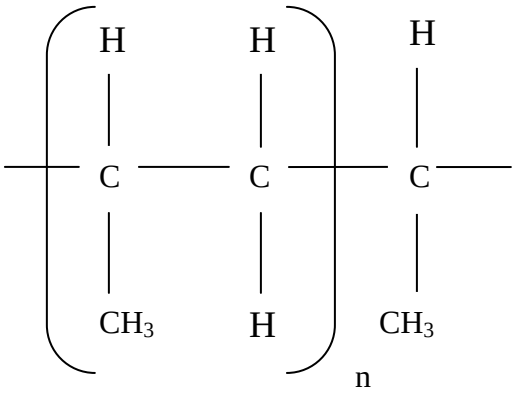

Figure 3.4 Polypropylene Chain (n is the number of polymerized unit)

Figure 3.5 Polypropylene of grade homo-polymer M110

Table 3.2 Properties of homo-polymer M110 polypropylene

Characteristic Property	Inferences
Density	0.92 gm/cc
Compressive strength	82 MPa
Tensile strength	46 MPa
Micro-hardness	0.55-0.65 GPa
Thermal conductivity	0.1 W/m-K
Glass transition temperature	-14.93°C
Coefficient of Thermal expansion	31.144 ppm /°C
Electrical conductivity	2.3 S/cm

3.1.2 Filler Material: (Titanium Dioxide)

Micro-sized titanium dioxide(TiO_2) is used as the filler material for the preparation of thermally conductive polymer composites in the present investigation. TiO_2 powders with average particle size of 90 -100 micron are supplied by Qualikems Ltd. It is the naturally occurring oxide form of titanium and occurs in nature as rutile, anatase or brookite. It is mainly sourced from ilmenite ore. This is the most widespread form of titanium dioxide bearing ore around the world. Rutile is the next most abundant form of titanium dioxide ore. The metastable anatase and brookitephases convert to rutile upon heating. TiO_2 is used as filler for its moderate thermal conductivity.

Table 3.3 Properties of filler materials (TiO_2)

Characteristic Property	Inferences
Density	4.197 gm/cc
Compressive strength	680 MPa
Tensile strength	367.5 MPa
Micro-hardness	8.63 GPa
Thermal conductivity	11.7 W/m-K
Coefficient of Thermal expansion	8.6 ppm /°C
Electrical conductivity	2.38 x10^6S/cm

Figure 3.6 Filler material (Titanium Dioxide)

A pictorial view of TiO_2 used in the present work is given in Figure 3.6 and Table 3.3 provides some of its important properties.

3.2. EXPERIMENTAL DETAILS

3.2.1. Composite Fabrication

3.2.1.1. Epoxy composites filled with titanium dioxide (Hand lay-up technique)

Composite samples of various compositions are prepared by hand lay-up technique. Hand lay-up technique is the oldest and simplest technique for composite fabrication. The epoxy-TiO_2 composites are prepared in the following steps (i) Uncured epoxy (LY556) and its corresponding hardener (HY 951) are mixed in a ratio of 10:1 by weight as per recommendation.(ii) Micro-sized TiO_2 powder is mixed with the epoxy in different proportions.(iii)The uniformly mixed dough (epoxy filled with TiO_2) is then slowly decanted into the glass molds so as to get both disc type specimens (diameter 50 mm and thickness 3 mm) and rectangular slab specimens (length 200 mm, width 200 mm, thickness 4 mm), coated beforehand with wax and a uniform thin film of silicone-releasing agent.(iv)The castings are then left at room temperature for about 24 hours and then the glass molds are broken and the samples are released. From this slab

circular disc and dog-bone shaped specimens are cut for different characterization tests. Two sets of samples are prepared according the above procedure. The compositions of set-1 and set-2 composites have been listed in Tables 3.4 and 3.5 respectively.

Table 3.4 Set-1 Epoxy-TiO_2 composites

Composition
Epoxy + 0 vol% TiO_2
Epoxy + 1.4 vol% TiO_2
Epoxy + 3.35 vol% TiO_2
Epoxy + 5.23 vol% TiO_2
Epoxy + 7.85 vol% TiO_2
Epoxy + 9.7 vol% TiO_2
Epoxy + 11.3 vol% TiO_2

Table 3.5 Set-2 Epoxy-TiO_2 composites

Composition
Epoxy + 0 vol % TiO_2
Epoxy + 2.5 vol % TiO_2
Epoxy + 5.0 vol % TiO_2
Epoxy + 7.5 vol % TiO_2
Epoxy + 10.0 vol% TiO_2
Epoxy + 12.5 vol% TiO_2
Epoxy + 15.0 vol% TiO_2
Epoxy + 17.5 vol% TiO_2
Epoxy + 20.0 vol% TiO_2
Epoxy + 22.5 vol% TiO_2
Epoxy + 25.0 vol% TiO_2

A schematic diagram of the fabrication process using hand lay-up technique for particulate filled epoxy composites is given in Figure 3.7. Figure 3.8 shows some of these composite samples prepared through this hand lay-up technique.

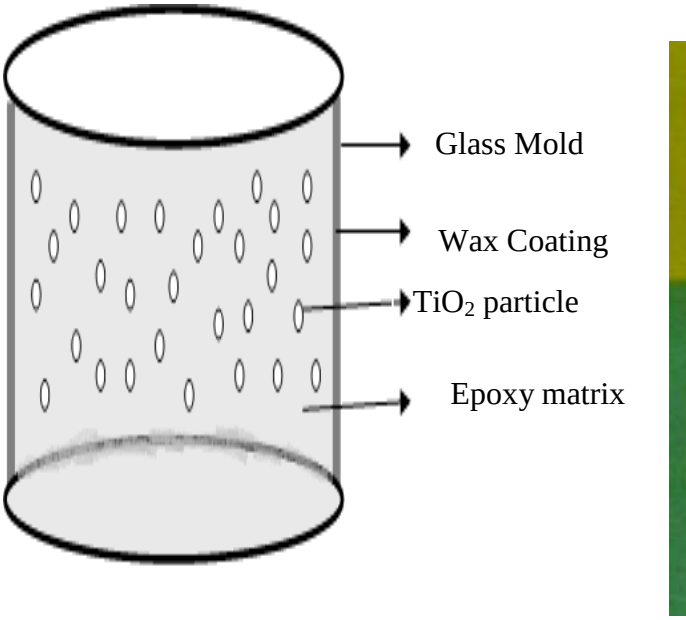

Figure 3.7 Particulate filled epoxy composite fabrication by hand lay-up process

Figure 3.8 Micro-sized titanium dioxide filled epoxy composites

3.2.1.2. Polypropylene composites filled with TiO_2 (Compression Molding Technique)

Similar sets of composites for 11 different compositions(Table 3.6) where filler content is ranging from 0 vol % to 25 vol% are fabricated by compression molding technique. Figure 3.9 shows some of these composite samples.

Table 3.6 Set-3 PP-TiO_2 composites

Composition
PP + 0 vol % TiO_2
PP + 2.5 vol % TiO_2
PP + 5.0 vol % TiO_2
PP + 7.5 vol % TiO_2
PP + 10.0 vol % TiO_2
PP + 12.5 vol % TiO_2
PP + 15.0 vol % TiO_2
PP + 17.5 vol % TiO_2
PP + 20.0 vol % TiO_2
PP + 22.5 vol % TiO_2
PP + 25.0 vol % TiO_2

Rheomix 600 batch mixer with chamber volume 90 cm^3 is used to melt and mix PP with $TiO_2$by the help of two rotor rotating in opposite direction. The temperature of the mixing chamber is set to 190^oC and time of the mixing is 10 minutes. The temperature and time differ for different sets of matrix filler combination. As the mixing is over, the material is taken out from the chamber and after cooling it is cut into small pieces. These uniformly mixed PP-TiO_2 composite pieces are then kept in a hot air oven for about an hour. These small pieces of materials are then taken out from the hot air oven and kept in compression molding die. The dimension of the die is 3 mm thickness and 60×60 mm^2area. By using a hydraulic press, the material is pressed with a pressure of 150 $kg/cm^2$for around three minutes. The temperature of the compression molding die is maintained at 190^oC with the help of heaters. After that it gets water cooled and the sheet is taken out from the die. Later the disc type specimens of required dimensions for experimentation are cut from the sheets. A picture of compression molding machine is shown in the Figure 3.10.

Figure 3.9 Micro-sized titanium dioxide filled polypropylene composites

Figure 3.10 Compression molding machine

3.3. CHARACTERIZATION

3.3.1 Physical Characterization

3.3.1.1Density

Density of a composite depends on the relative proportion of matrix and reinforcing materials and it is one of the most important factors for determining the properties of the composites. The theoretical density (ρ_{ct})of composite materials in terms of weight fractions of different constituents can easily be obtained using the following equation given by Agarwal and Broutman[132].

$$\rho_{ct} = 1 \Big/ \left\{ \left(\frac{w_f}{\rho_f} \right) + \left(\frac{w_m}{\rho_m} \right) \right\} \quad \textbf{(3.1)}$$

where, w and ρ represent the weight fraction and density respectively. The suffixes f and m stand for the filler and matrix respectively. The actual density (ρ_{ce}) of the composite can be determined experimentally by the Archimedes principle i.e. the water displacement technique (ASTM D 792-91).

The volume fraction of voids (v_v) in the composites is calculated by using the following equation:

$$v_v = \left(\rho_{ct} - \rho_{ce} \right) \Big/ \rho_{ct} \quad \textbf{(3.2)}$$

3.3.1.2 Scanning Electron Microscopy

The micro-structural features of the various particulate filled composite specimens are examined by Scanning Electron Microscope JEOL JSM-6480 LV (Figure 3.11). The specimens are mounted on stubs with silver paste. To improve the penetration of light and for better surface micrographs, a thin film of platinum is vacuum-evaporated onto the samples before the micro graphs are taken.

Figure 3.11 Scanning Electron Microscope (JEOL JSM-6480LV)

Figure 3.12 Leitz micro-hardness tester

3.3.2 Mechanical Characterization

3.3.2.1Micro-hardness

Micro-hardness measurement is done using a Leitz micro-hardness tester (Figure 3.12). A diamond indenter, in the form of a right pyramid with a square base and an angle 136° between opposite faces, is forced into the material under a load *F*. The two diagonals *X* and *Y* of the indentation left on the surface of the material after removal of the load are measured and their arithmetic mean is calculated. In the present study, the load considered is *F*= 0.2454 N and Vickers hardness number is calculated using the following equation.

$$H_v = 0.1889\frac{F}{L^2}$$

where, $$L = \frac{X+Y}{2} \quad \textbf{(3.3)}$$

where, *F* is the applied load (N), *L* is the diagonal of square impression (mm), *X* is the horizontal length (mm) and *Y* is the vertical length (mm). The composite hardness is finally expressed in GPa.

3.3.2.2 Compressive strength

The cured composite samples of required dimension (length 10 mm, diameter 10 mm), are used for the uni-axial compression test as per ASTM D695standard [133]. This helps to avoid buckling, reduce friction due to small cross-sectional area, avoid premature failure due to sharp corners and prevent self-reaction of the epoxy resin during curing. Static uni-axial compression tests are carried out on these specimens using Universal Testing Machine *Instron 1195* (Figure 3.13). The loading arrangement is shown in Figure 3.14a. A typical sample used for compression test is shown in Figure 3.15b. Four identical specimens are tested for each composition and the average result is recorded as the compressive strength of the composite. The crosshead speed is maintained constant at 1mm/min and the compression is stopped when the specimen shows signs of failure or when densification is complete.

3.3.2.3Tensile strength

The cured dog bone shaped composite samples of required dimension (length 150mm, end width 20mm and mid width 12 mm) are used for the tensile test as per ASTM E 1309 standard. An uni-axial load is applied through both the ends. In the present work, this test is performed in the same universal testing machine Instron 1195 at a cross head speed of 10 mm/minute and the results are used to calculate the tensile strength of the composite samples. The loading arrangement is shown in Figure 3.15b. A typical dog-bone shaped sample used for tensile test is shown in Figure 3.15a. In this case also, the test is repeated four times on each composite type and the mean value is reported as the tensile strength of that composite.

3.3.3 Thermal Characterization

3.3.3.1Thermal Conductivity: Experimental Determination

Unitherm^{TM} Model 2022 thermal conductivity tester is used to measure the thermal conductivity of various materials, which include polymers, glasses, ceramics, rubbers, composites, few metals and other materials with medium to low thermal conductivity. In the present work, this instrument is used to measure the room temperature effective thermal conductivity of the composite specimens. Disc type specimens (diameter = 50 mm, thickness = 3 mm) are used for this purpose. This test is conducted in accordance with ASTM E-1530standards. The pictorial view of the Unitherm^{TM} Model 2022 tester is given in Figure 3.16.

Operating Principle of Unitherm^{TM} Model 2022

The material is held under uniform compressive load between two polished surfaces, each controlled at different temperatures. The lower surface is part of a calibrated heat flow transducer. The heat flows from the upper surface, through the sample, to the lower surface, establishing an axial temperature gradient in the stack. After reaching thermal equilibrium, the temperature difference across the sample is measured along with the output from the heat flow transducer. These values and the sample thickness are then used to calculate the thermal conductivity. The temperature drop through the sample is measured with

temperature sensors in the highly conductive metal surface layers on either side of the sample.

By definition "Thermal conductivity is the exchange of energy between adjacent molecules and electrons in a conducting medium, it is a material property that describes heat flow within a body for a given temperature difference per unit area."

For one-dimension heat flow, the equation is given as:

$$Q = \kappa A \frac{T_1 - T_2}{x} \quad \textbf{(3.4)}$$

where, Q is the heat flux (W), A is the cross-sectional area (m^2), k is thermal conductivity (W/m-K), x is the sample thickness (m), $T_1 - T_2$ is the temperature difference between surfaces (°C or K).

The thermal resistance of the sample is given as:

$$R = \frac{T_1 - T_2}{QA} \quad \textbf{(3.5)}$$

where, R is sample resistance between hot and cold surfaces. (m^2-K / W).

From the former equation, we can write

$$k = \frac{x}{R} \quad \textbf{(3.6)}$$

In Unitherm™ 2022, transducers measure the value of heat flux Q and the temperature difference between upper and lower plate. Thus, thermal resistance between surfaces can be evaluated. Providing different thickness and known cross-sectional area as input parameters, the sample thermal conductivity can be calculated.

Figure 3.13 Universal testing machine *Instron 1195*

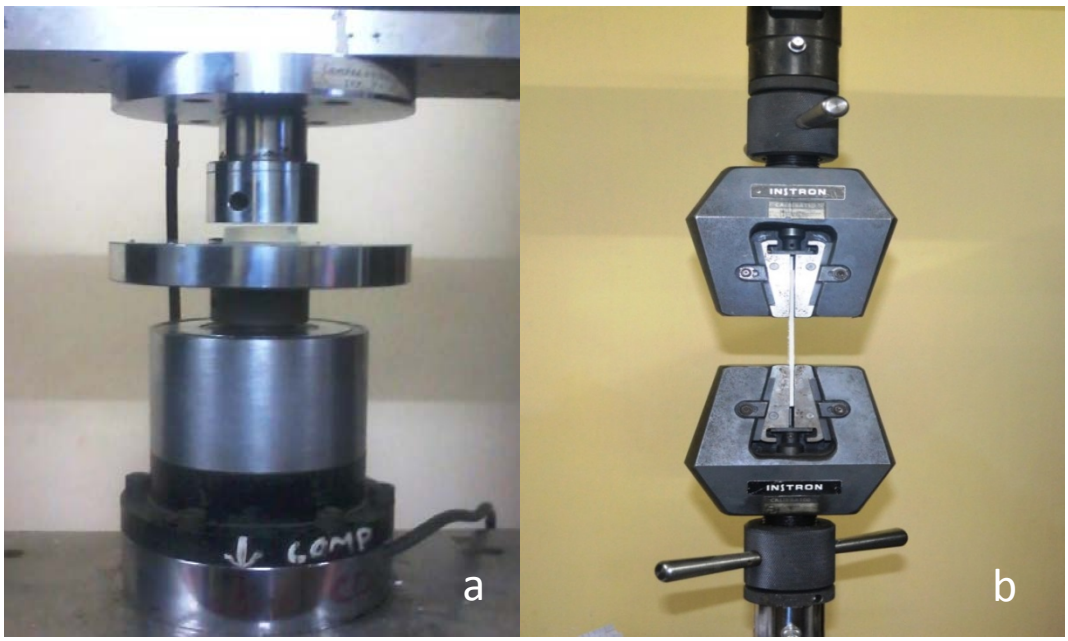

Figure 3.14 (a) Loading arrangement for compression test
(b) Loading arrangement for tensile test

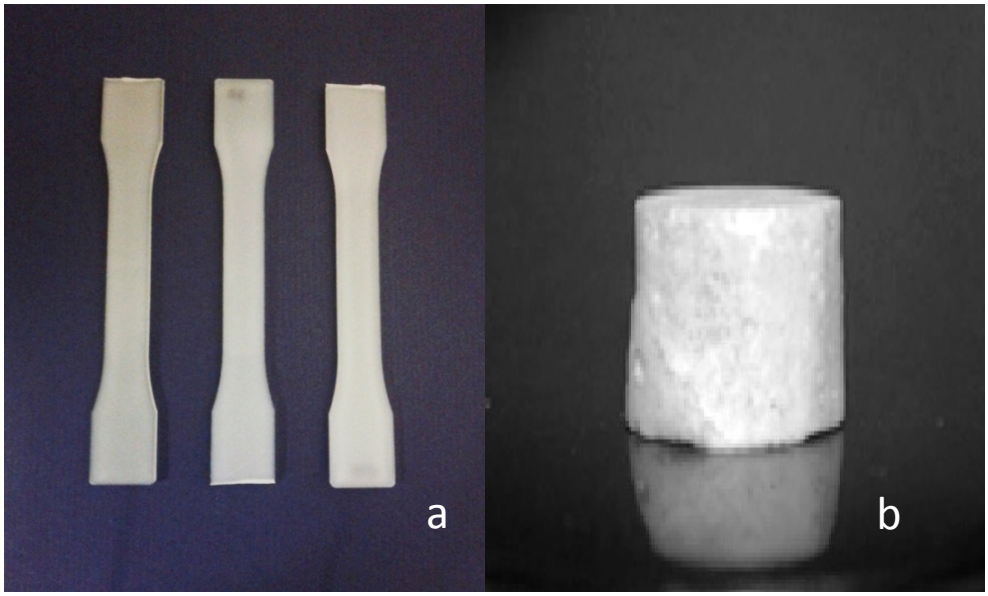

Figure 3.15 (a) Typical composite specimens for tensile test
(b) Typical composite specimens for compression test

Figure 3.16 Thermal conductivity tester*Unitherm*^{TM}*2022*

Figure 3.17 Perkin Elmer DSC-7 Thermal Mechanical Analyzer

3.3.3.2 Thermal Mechanical Analyzer

Glass transition temperature (T_g) is the temperature at which the mechanical properties of amorphous polymer changes from the brittle state of glass to a rubbery state. The most important property change at the glass transition temperature of the printed circuit board (PCB) materials is the thermal expansion, which is a swift from a relative low value to a very high value. This kind of change is not desirable as it imposes stress on the PCBs when they experience high-temperatures during manufacturing, assembly or during their service-life. Similarly, coefficient of thermal expansion (CTE) is the rate of change of the thermal expansion of a material. A material with high CTE will induce stress within the component. A low CTE is therefore preferable. In the present work, T_g and CTE of the composites are measured with a *Perkin Elmer DSC-7 Thermal Mechanical Analyzer* (TMA) in expansion mode (Figure 3.17). At first, the TMA sample stage is purged with nitrogen gas. The sample length is set between 6-8 mm and the width as well as thickness is about 2-3mm. During the TMA measurement, the specimen is heated from 30 to 150°C at a heating rate of 5°C/min. For each measurement, two heating scans are used. The first

heating scan is used to eliminate any possible internal stress and moisture in the sample which is likely to be generated during the curing and sample preparation processes. The second heating scan is used to determine the T_g and the CTE of the material.

Chapter Summary

This chapter has provided:

- The description of materials (matrix and fillers) used in this research
- The details of fabrication and characterization of the composites
- The details of thermal property measurement

The next chapter presents the test results related to the physical and mechanical properties of the polymer composites under this study.

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Chapter 4

Results and Discussion – I

PHYSICAL AND MECHANICAL CHARACTERISTICS OF THE COMPOSITES

This chapter presents the measured values of the physical and mechanical properties of the epoxy and polypropylene composites filled with micro-sized TiO_2particles. The relative effects of TiO_2 particles on various physico-mechanical properties of epoxy and polypropylene (PP) composites have also been discussed. It also presents scanning electron micrographs showing some typical micro-structural features of the composites under this study.

4.1 PHYSICAL CHARACTERISTICS

4.1.1 Density and volume fraction of voids

The theoretical and measured densities along with the corresponding volume fraction of voids in the epoxy-TiO_2 and PP-TiO_2 composites are presented in Tables 4.1 and 4.2 respectively. It may be noted that the composite density values calculated theoretically from weight fractions using Eqn.3.1 are not equal to the experimentally measured values. This difference is a measure of voids and pores present in the composites. It is found that with the increase in TiO_2 micro-particles content in epoxy resin from 0 to 25vol%, there is a rise in density of the composite by about 47.54% although there is a simultaneous increase in the void fraction or porosity from 4.41 % to 13.39% (Table 4.1). Similarly, a substantial rise in composite density by about 78.26% is observed as the TiO_2 micro-particle content in polypropylene increased from 0 to 25 vol%. For the PP-TiO_2composite with TiO_2 content of 25 vol%, the volume fraction of voids is estimated to be as high as 3.35% (Table 4.2).

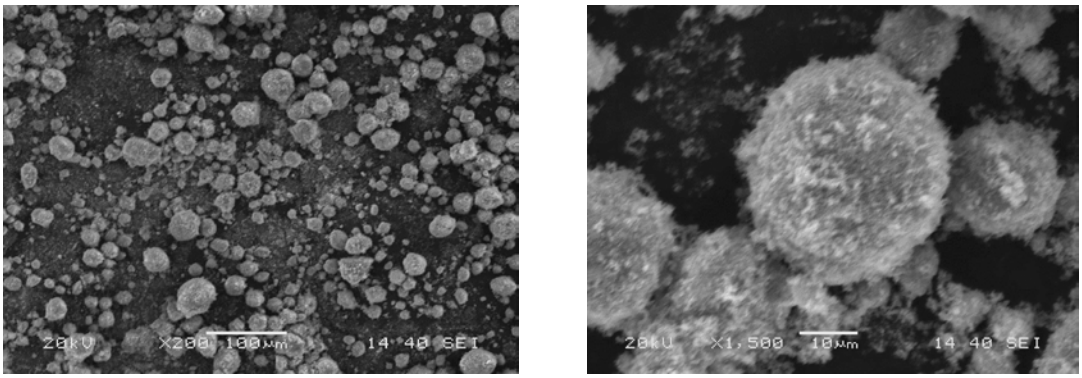
Table 4.1 Measured and Theoretical densities of the composites (Epoxy filled with TiO_2)

Composites	Measured density (gm/cc)	Theoretical density (gm/cc)	Void fraction (%)
Epoxy + TiO_2 (02.5 vol%)	1.125	1.177	4.41
Epoxy + TiO_2 (05.0vol%)	1.196	1.254	4.62
Epoxy + TiO_2 (07.5 vol%)	1.246	1.332	6.45
Epoxy + TiO_2 (10.0vol%)	1.295	1.409	8.09
Epoxy + TiO_2 (12.5 vol%)	1.345	1.487	9.54
Epoxy + TiO_2 (15.0 vol%)	1.401	1.564	10.48
Epoxy + TiO_2 (17.5 vol%)	1.466	1.640	10.60
Epoxy + TiO_2 (20.0 vol%)	1.502	1.719	12.62
Epoxy + TiO_2 (22.5 vol%)	1.552	1.790	13.21
Epoxy + TiO_2 (25.0 vol%)	1.623	1.874	13.39

Table 4.2 Measured and Theoretical densities of the composites (Polypropylene filled with TiO_2)

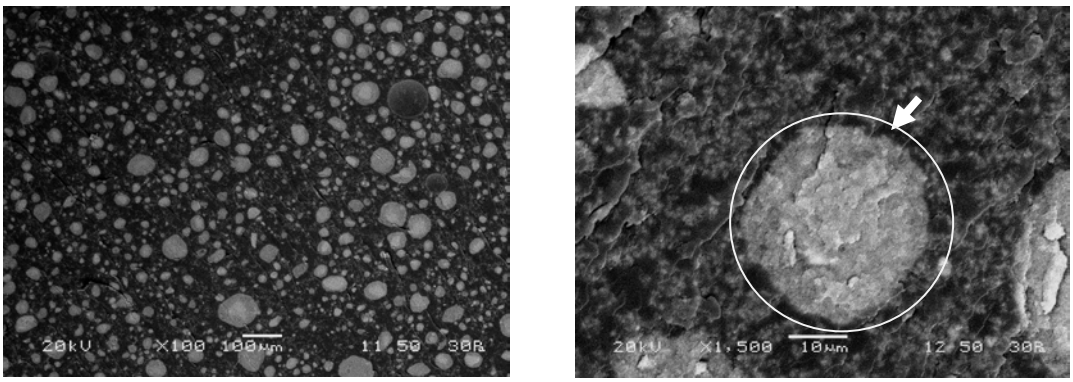
Composites	Measured density (gm/cc)	Theoretical density (gm/cc)	Void fraction (%)
Polypropylene + TiO_2 (02.5vol%)	0.992	1.000	0.8
Polypropylene + TiO_2 (5.0vol%)	1.072	1.083	1.01
Polypropylene + TiO_2 (7.5 vol%)	1.153	1.165	1.71
Polypropylene + TiO_2 (10 vol%)	1.216	1.240	1.93
Polypropylene + TiO_2 (12.5vol%)	1.302	1.329	2.03
Polypropylene + TiO_2 (15 vol%)	1.379	1.411	2.26
Polypropylene + TiO_2 (17.5vol%)	1.456	1.503	2.52
Polypropylene + TiO_2 (20vol%)	1.530	1.575	2.85
Polypropylene + TiO_2 (22.5vol%)	1.550	1.600	3.12
Polypropylene + TiO_2 (25 vol%)	1.640	1.700	3.53

Density of a composite depends on the relative proportion of matrix and reinforcing materials and this is one of the most important factors determining the properties of the composites. The void content is the cause for the difference between the values of true density and the theoretically calculated ones. The voids significantly affect some of the mechanical properties and even the performance of the composites in the workplace. Higher void content usually mean lower fatigue resistance, greater susceptibility to water penetration and weathering [132]. The knowledge of void content is desirable for better estimation of quality of the composites. It is understandable that a good composite should have fewer voids. However, presence of void is unavoidable particularly in composites made through hand-lay-up route.



(a) (b)

Figure 4.1 SEM images of micro-sized TiO_2 particles used as filler material



(a) (b)

Figure 4.2 Some typical SEM images of particulate-filled epoxy composites

4.1.2 Micro-structural characterization

It is well known that the properties of the composites are strongly dependent on the interaction of the filler and the matrix. In order to evaluate this interaction, the microstructure of the composites, including the dispersion of the micro-sized TiO_2 particles in the epoxy matrix are observed under scanning electron microscope. Figure 4.1a shows a typical SEM image of raw TiO_2 particles used as the particulate filler in the present work. A single filler at a higher magnification is shown in Figure 4.1b. These micrographs confirm the spherical shape of the filler particles i.e. TiO_2used as reinforcement in the polymer resin.

The surface morphologies of TiO_2 filled epoxy composites are shown in Figures 4.2.aand 4.2b. It is seen from these micrographs that micro-particles are exposed on the fracture surface or peeled from the matrix to form holes or embedded in the matrix and the dispersion of these micro-particles within the polymer matrix is reasonably uniform.

4.2 MECHANICAL CHARACTERIZATION

4.2.1 Composite Micro-hardness

Hardness is considered as one of the most important characteristic features of a multi-component composite system as it indicates the ability of the composite to resist indentation. In the present work, micro-hardness values are measured and the test results for the epoxy-TiO_2 and PP-TiO_2composites are presented in Tables 4.3 and 4.4 respectively. It is evident that with addition of TiO_2,micro-hardness of the composites is improved and this improvement is a function of the TiO_2 content. With 25vol% of TiO_2 addition, the hardness is improved by about 7 times. Similarly, for PP-TiO_2composites also, with the increase in TiO_2 content, the composite micro-hardness is found to be increasing although the rate of improvement is not as high as in the case of epoxy-TiO_2 composites. While the hardness of neat polypropylene is 0.085 GPa, that of the PP-TiO_2composite with 25 vol% of TiO_2 comes out to be only 0.492GPa indicating an improvement of about 6 times. This difference in hardness is obvious as the neat hardened epoxy is much harder than neat PP.

Table 4.3 Mechanical properties of the composites (Epoxy filled with TiO_2)

Composites	Tensile strength (MPa)	Compressive strength (MPa)	Micro-hardness (GPa)
Neat Epoxy (hardened)	58.00	90.00	0.085
Epoxy + TiO_2 (02.5 vol%)	57.90	90.20	0.112
Epoxy + TiO_2 (05.0 vol%)	57.32	90.56	0.196
Epoxy + TiO_2 (07.5 vol%)	56.60	91.03	0.247
Epoxy + TiO_2 (10.0 vol%)	55.97	91.56	0.292
Epoxy + TiO_2 (12.5 vol%)	55.23	92.12	0.344
Epoxy + TiO_2 (15.0 vol%)	54.74	92.48	0.397
Epoxy + TiO_2 (17.5 vol%)	54.00	92.95	0.468
Epoxy + TiO_2 (20.0 vol%)	53.50	93.23	0.499
Epoxy + TiO_2 (22.5 vol%)	53.04	93.78	0.547
Epoxy + TiO_2 (25.0 vol%)	52.56	94.28	0.582

Table 4.4 Mechanical properties of the composites (Polypropylene filled with TiO_2)

Composites	Tensile strength (MPa)	Compressive strength (MPa)	Micro-hardness (GPa)
Neat Polypropylene	46.00	82.00	0.076
Polypropylene+ TiO_2(2.5 vol%)	45.86	82.12	0.102
Polypropylene+ TiO_2(5.0vol%)	45.65	82.56	0.155
Polypropylene+ TiO_2(7.5 vol%)	45.46	82.73	0.218
Polypropylene+ TiO_2(10.0vol%)	45.23	82.97	0.295
Polypropylene+ TiO_2(12.5 vol%)	45.03	83.16	0.324
Polypropylene+ TiO_2(15.0vol%)	44.67	83.43	0.358
Polypropylene+ TiO_2(17.5 vol%)	44.22	83.96	0.399
Polypropylene+ TiO_2(20.0vol%)	43.97	84.26	0.423
Polypropylene+ TiO_2(22.5 vol%)	43.48	84.72	0.447
Polypropylene+ TiO_2(25.0vol%)	42.88	85.65	0.492

4.2.2 Compressive Strength

Compressive strengths of the composite specimens are evaluated by conducting uni-axial compression test and the test results for the epoxy-TiO_2 and PP-TiO_2 composites are presented in Tables 4.3 and 4.4 respectively. It is noticed that with addition of TiO_2, compressive strength of the composite is improved and this improvement is a function of the TiO_2 content. While the compressive strength of neat epoxy is 90MPa, it increases by about 5% to 94.28 MPa with the incorporation of 25 vol% of TiO_2 in it. But in case of PP-TiO_2 composites, although the compressive strength is found to be increasing with TiO_2 content, the improvement is not as high as in the case of epoxy-TiO_2 composites. Here, an enhancement of only about 4% in compressive strength is recorded with a TiO_2 content of 25 vol%. Measured compressive strength values of the both epoxy-TiO_2 and PP-TiO_2composites filled with TiO_2 in different proportions are also graphically illustrated in Figure 4.3 which shows a gradual increase in compressive strength values with increase in filler content.

4.2.3 Tensile Strength

Tensile strengths of the composite specimens are evaluated and the test results for the epoxy-TiO_2 and PP-TiO_2 composites are presented in Tables 4.3 and 4.4 respectively. It is noticed that with addition of TiO_2, tensile strength of the composite decreases and this decrement is a function of the filler content. While the tensile strength of neat epoxy is 58 MPa, it decreases by about 9.3 % to 52.56MPa with the incorporation of 25 vol% of TiO_2 in it. In case of PP-TiO_2 composites too, the tensile strength is found to be decreasing with TiO_2content and the reduction is less as compared to that in case of the epoxy-TiO_2 composites. Here, a reduction of about 6.7% in the tensile strength is recorded with a TiO_2 content of 25 vol%. Measured tensile strength values of both epoxy and polypropylene composites filled with TiO_2 in different proportions are also graphically illustrated in Figure 4.4 which shows a gradual decrease in tensile strength values with increase in filler content.

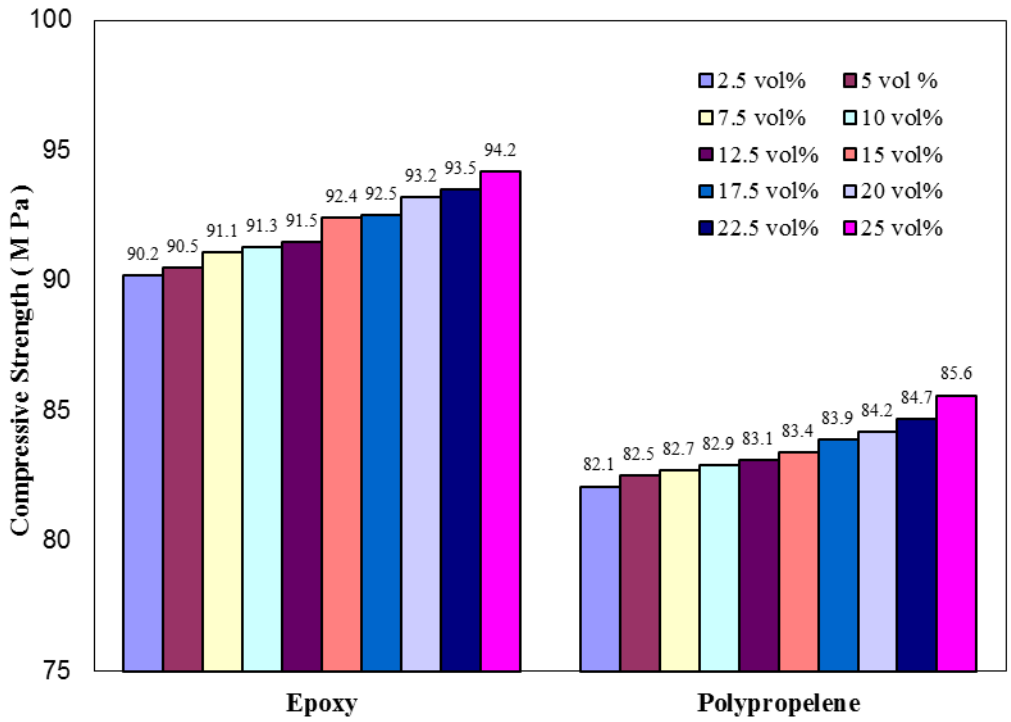


Figure 4.3 Variation of compressive strength with TiO_2content

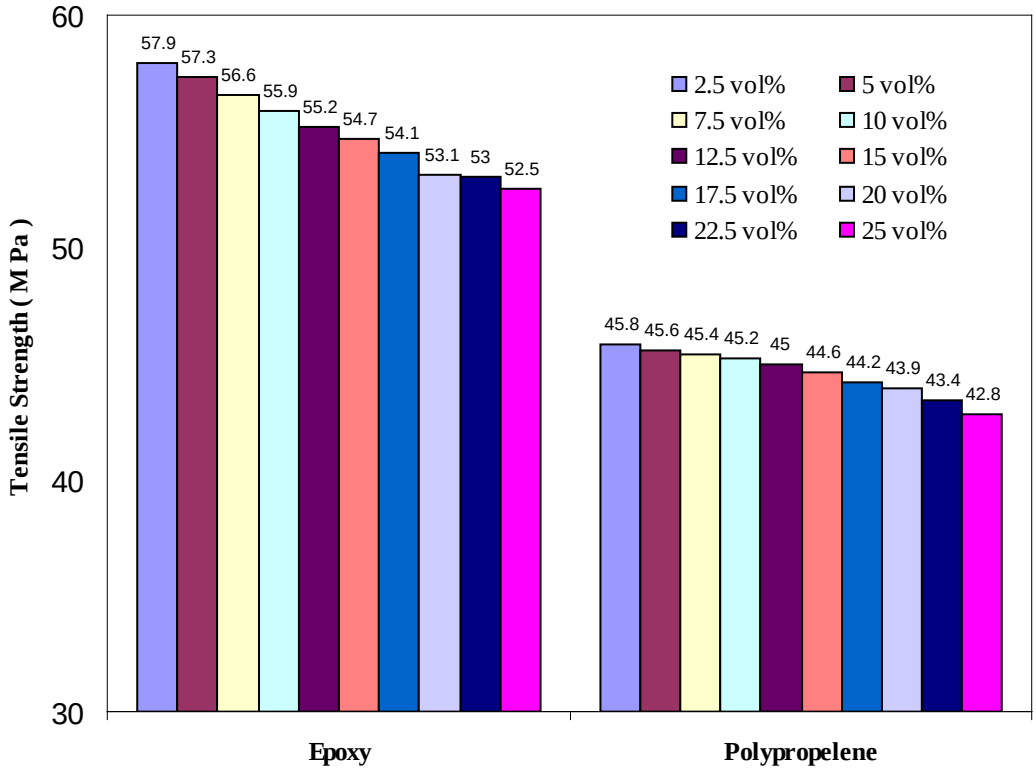


Figure 4.4 Variation of tensile strength with TiO_2content

Discussion

Density of the particulate filled composites under this study is always higher than that of the matrix polymer sinceTiO_2 particles are denser than both epoxy and polypropylene. Further, incorporation of filler leads to the improvement of mean composite hardness. Mechanical characterization of the composites under this investigation reveals that the trends observed in respect to the compressive strengths are quite different from those obtained in the case of tensile strength variations with the filler loading (Tables 4.3 and 4.4). The increase in compressive strength with increased filler content is due to the favorable deformation processes facilitated by the presence of filler in both the matrices. Under a compressive loading situation, the fillers apparently aid the load bearing capability of a composite, rather than acting as stress raiser as in the case of tensile loading. Further, the fact that in a compression test, any crack or flaw introduced by the dispersion of the fillers gets healed/closed, contrary to the crack opening mechanism occurring in a tensile loading situation.

Chapter Summary

Several important conclusions emerge from the extensive results obtained in these studies carried out on epoxy and polypropylene composites filled with micro-sized titanium dioxide particles in regard to their physical, mechanical and micro-structural characteristics. The results presented in this chapter clearly indicate a trendy characterization in the behaviour of different particulate composites studied and they provide a very important criterion for the choice of the composites for specific needs.

The next chapter presents the test results related to the thermal characteristics of the composites filled with micro-sized TiO_2 particles with emphasis on their heat conduction capabilities.

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Chapter 5

Results and Discussion – II

THERMAL CHARACTERISTICS OF THE EPOXY-TiO_2 COMPOSITES

This chapter presents the test results for thermal properties such as effective thermal conductivity (k_{eff}), glass transition temperature (T_g) and coefficient of thermal expansion (CTE) of all the epoxy-TiO_2 composites under this investigation. The results of the numerical analysis and validation of the proposed theoretical models in regard to the determination of effective thermal conductivity are presented in this part of the thesis. This chapter also explores the consequence of inter-connectivity among the fillers in the epoxy matrix, leading to higher k_{eff}. The effects of particulate fillers on T_g and CTE of the composites are discussed.

5.1 EFFECTIVE THERMAL CONDUCTIVITY (k_{eff})

Effective thermal conductivities of epoxy composites filled with TiO_2 fillers are evaluated theoretically and experimentally. The interpretation and comparison of results obtained from different methods for composites with different filler concentrations are presented.

5.1.1. Numerical Methods :*Concept of Finite Element Method and ANSYS*

The finite element method was first developed in 1956 by Turner et al. [134] for the analysis of structural problems in aviation industry. Thereafter, the method was recognized for potential application in different types of applied sciences and engineering problems. Today, it is considered as one of the best methods for solving a wide variety of real world engineering problems. The basic idea in the

finite element method (FEM) is to find the solution of a complex engineering problem by replacing it with a simpler one. Since the actual problem is replaced by a simpler one in finding the solution, one is able to find only an approximate solution rather than an exact solution.

In FEM, the actual continuum of matter is represented as an assemblage of subdivisions called finite elements. These elements are considered to be interconnected at specific points called nodes. The nodes generally lie on the element boundaries where adjacent elements are considered to be connected. Since the actual variation of field variables such as displacement, temperature, stress, pressure, velocity etc. inside the continuum is not known, it is assumed that the variation of field variables inside a finite element can be approximated by a simple function. These approximating functions called interpolation models are defined in terms of the values of the field variable at the nodes. When the equilibrium equation for the whole continuum is written, the new unknowns will be the nodal values of the field variable. By solving the field equations, which are generally in matrix form, the nodal values of the field variable will be known. Once these are known, the approximating functions define the field variable throughout the assemblage of elements. A general purpose finite element modeling package called ANSYS is used for solving a wide variety of mechanical problems which entails to static/dynamic, structural analysis (both linear and non-linear), heat transfer and fluid flow problems as well as acoustic and electromagnetic problems.

Basic Steps in Finite Element Method

Solving a general engineering problem in FEM involves the following steps:

- The first step in the finite element method is to divide the structure or continuum into subdivisions or elements. Then the structure is to be modeled with suitable finite elements. The size, shape, arrangement and number of elements are to be decided in the first step.

- In the second step, a proper interpolation model is to be selected. Since the solution of a complex structure under any specified conditions cannot be predicted exactly, a suitable solution within an element is assumed to approximate the unknown solution. The assumed solution must be simple from a computational standpoint, but it should satisfy certain convergence requirements
- In the third step, element characteristic matrices and input data are to be derived from the assumed interpolation model by using either equilibrium conditions or a suitable vibrational principle.

Description of the problem:

The estimation of effective properties of composites is of vital importance for proper design and application of composite materials. The micro-structural characteristics are essential criteria which influence the effective properties of the composite. Micro-structure means the shape, size, spatial distribution and orientation of the embedment in the matrix. Despite the fact that most composite systems have inclusions of random distribution and orientation, a great insight of the effect of microstructure on the effective properties can be achieved from the analysis of composites with periodic structure. A system with high degree of symmetry in its structure is preferred as it can be easily analyzed. Based on micro-structure, composites can generally be classified as laminate composite, i.e. with multi-layered structure and dispersion composite, i.e. including a matrix phase and one or more dispersion phases. In this work, models of dispersion composites are generated. The factors affecting the effective thermal conductivity of dispersion composite are structural features of the composite and thermal conductivity of each component material. The structural features include shape and size of matrix, and volume fraction, shape, size and orientation of dispersion. The structure of dispersion composite is considered to be composed of some very simplified basic models. In a basic model, the shape of composite is assumed to be cubical.

A schematic representation of TiO_2 embedded in an epoxy body having a periodic arrangement is shown in Figure 5.1. The prescribed boundary conditions with the direction of heat flow for the conduction problem is shown in Figure 5.2 in which the temperature at the nodes along the surface ABCD is T_1 (=100^0C), the ambient convective heat transfer coefficient is assumed to be 25 W/m^2-K and the analysis of the problem is done at a room temperature of 27°C. The other surfaces parallel to the direction of the heat flow are assumed to be adiabatic. The temperatures at the inside domain and on the other boundaries are not apprehended. A few presumptions involved in this analysis are:

- The composites are macroscopically homogeneous.
- Locally both the matrix and filler are homogeneous and isotropic.
- The thermal contact resistance between the filler and the matrix is negligible.
- The composite body is free from voids.
- The fillers are assumed to be uniformly distributed in the matrix in a square periodic array.

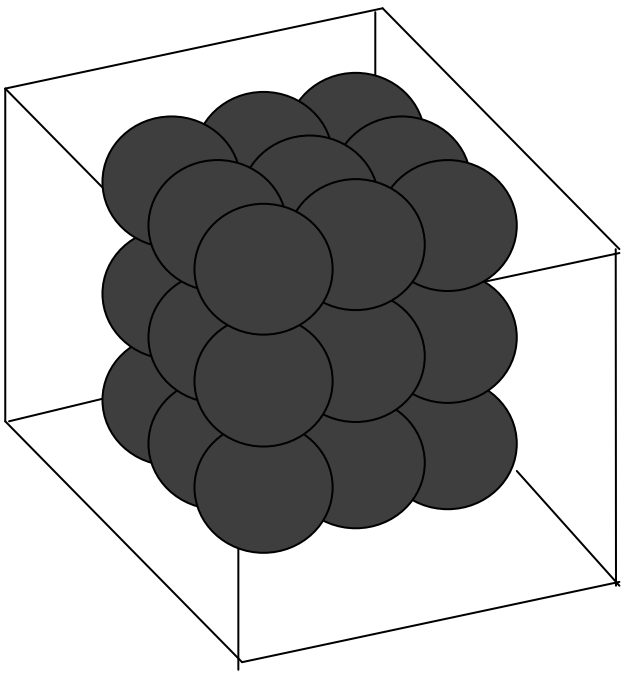

Figure 5.1 A three dimensional sphere-in-cube arrangement

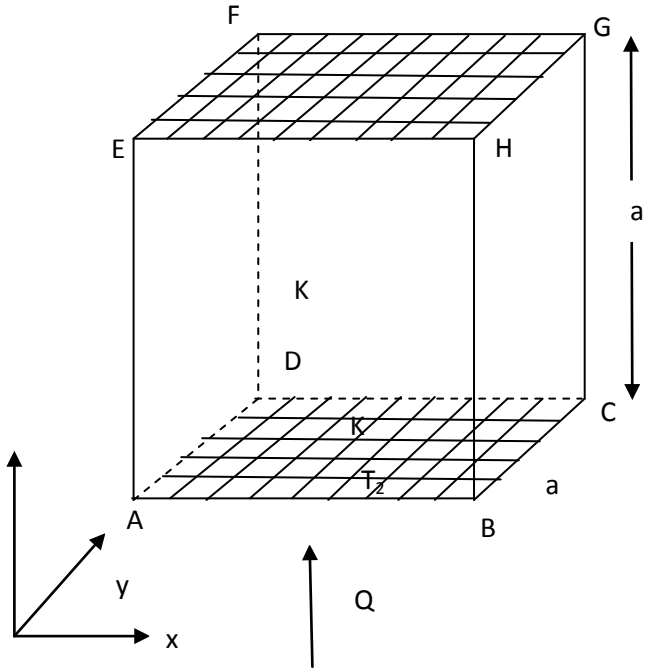

Figure 5.2 The heat flow direction and boundary conditions for the particulate-polymer composite

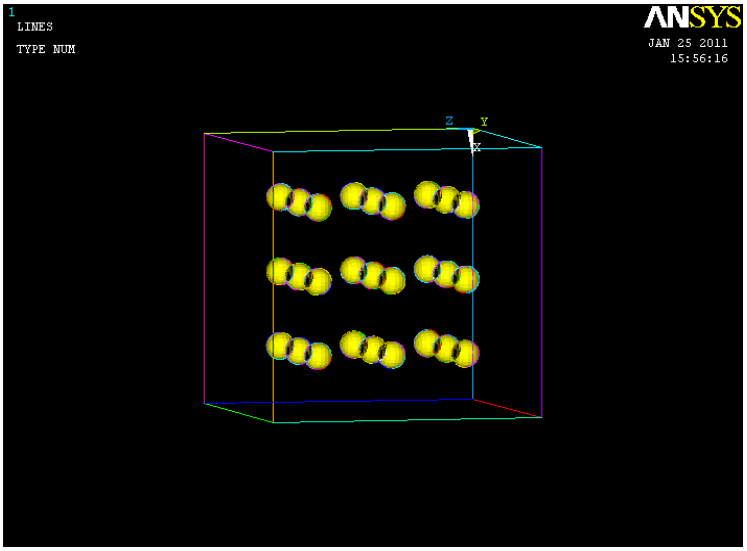

Figure 5.3 A typical 3-D sphere-in-cube model in ANSYS

Thermal conductivities of the TiO_2-epoxy composites are numerically estimated by using the sphere-in-cube model. A typical 3-D physical model showing arrangement of TiO_2 micro-spheres (1.4 vol %) within the cube shaped matrix body is illustrated in Figure 5.3. Temperature profiles obtained from FEM analysis for these composites with TiO_2 concentrations of 1.4, 3.35, 5.23, 7.85, 9.42 and 11.3 vol% are presented in Figures 5.4a, 5.4b, 5.4c, 5.4d, 5.4e and 5.4f respectively.

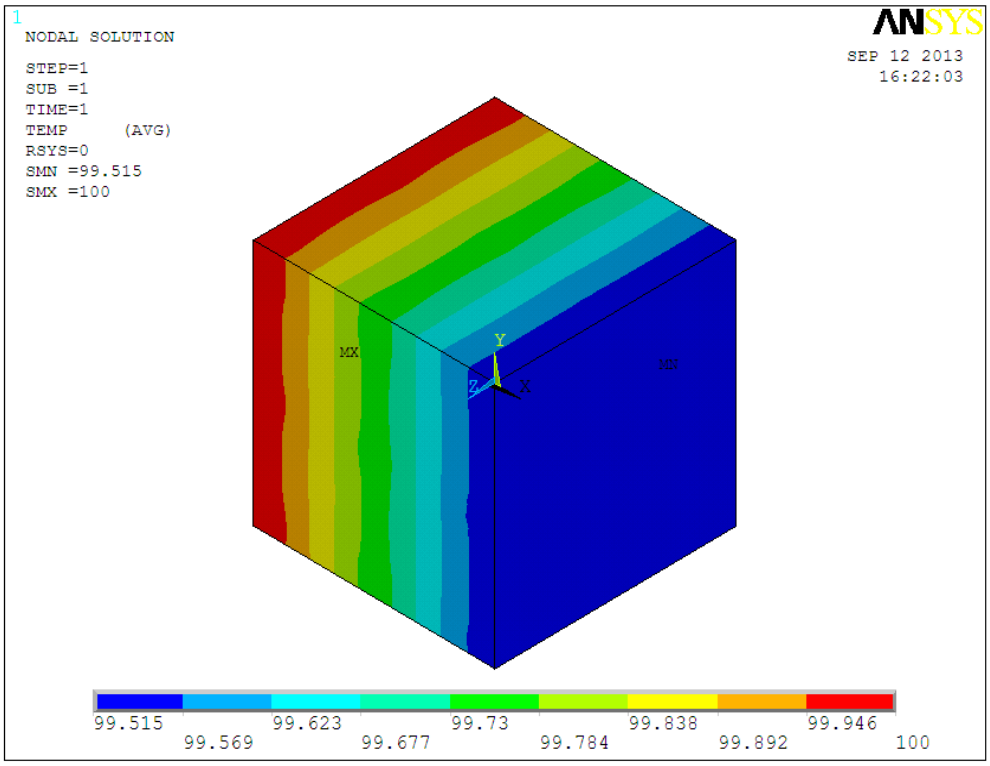

Figure 5.4a Temperature profile obtained for epoxy filled with 1.4 vol % TiO_2

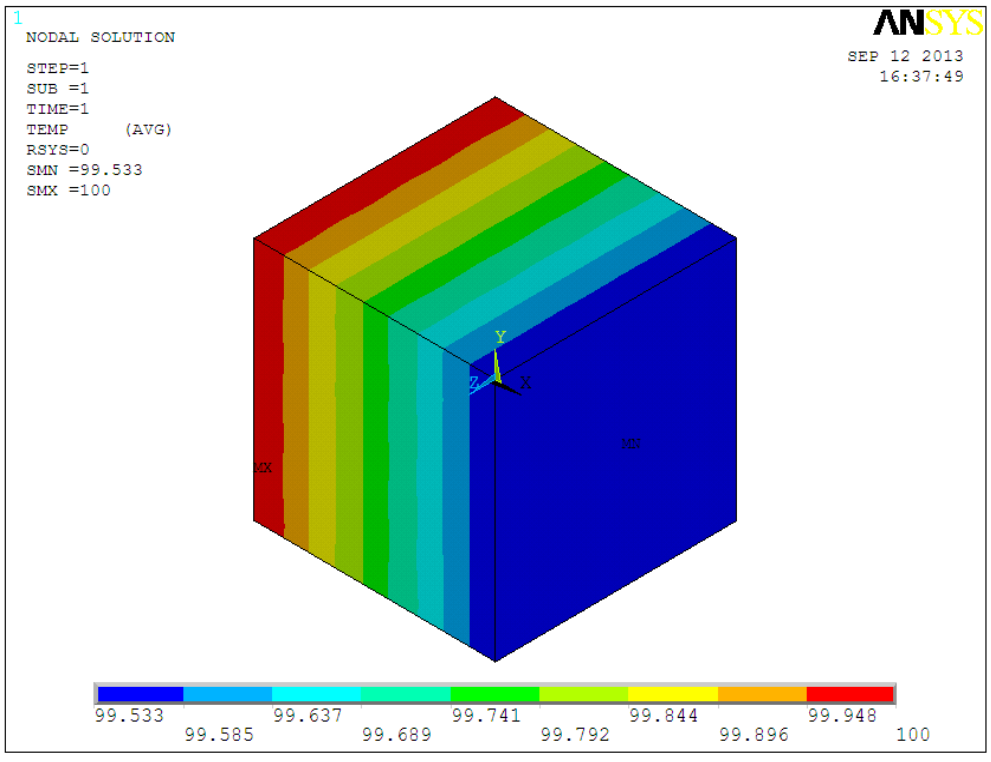

Figure 5.4b Temperature profile obtained for epoxy filled with 3.35vol % TiO_2

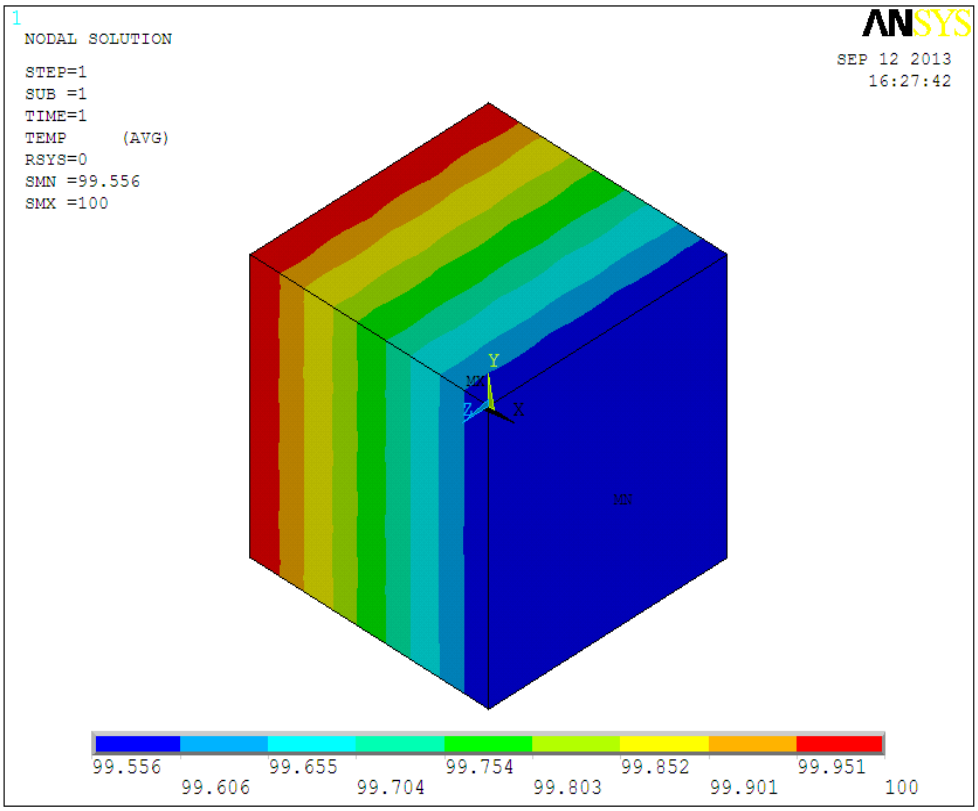

Figure 5.4c Temperature profile obtained for epoxy filled with 5.23 vol% TiO_2

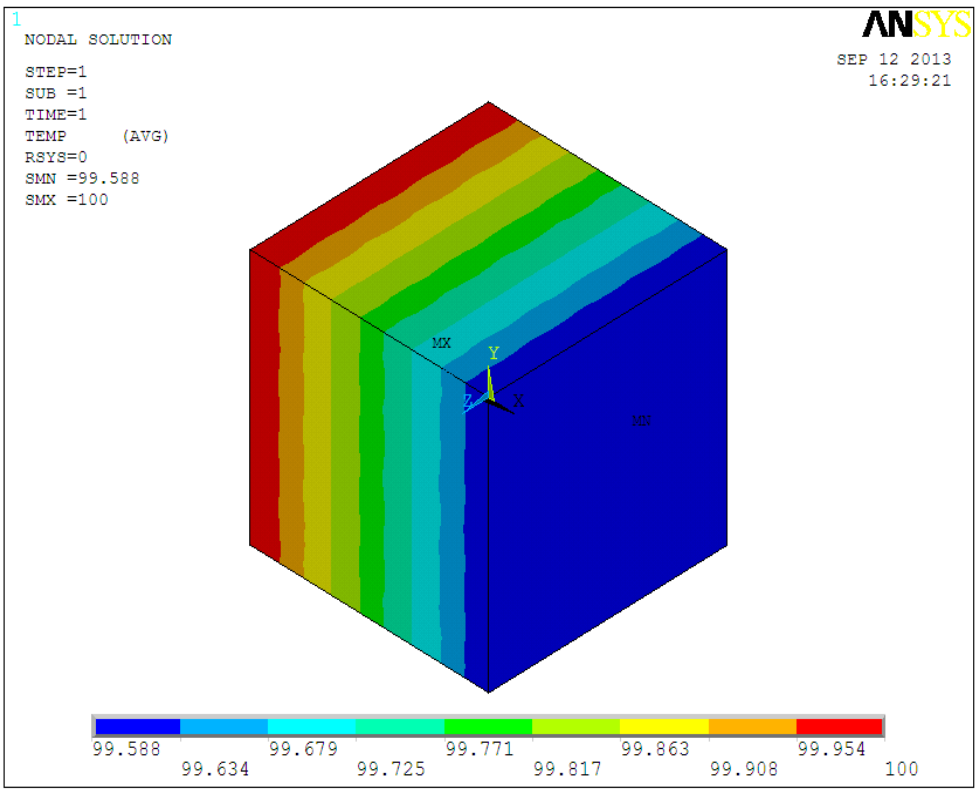

Figure 5.4d Temperature profile obtained for epoxy filled with 7.85 vol % TiO_2

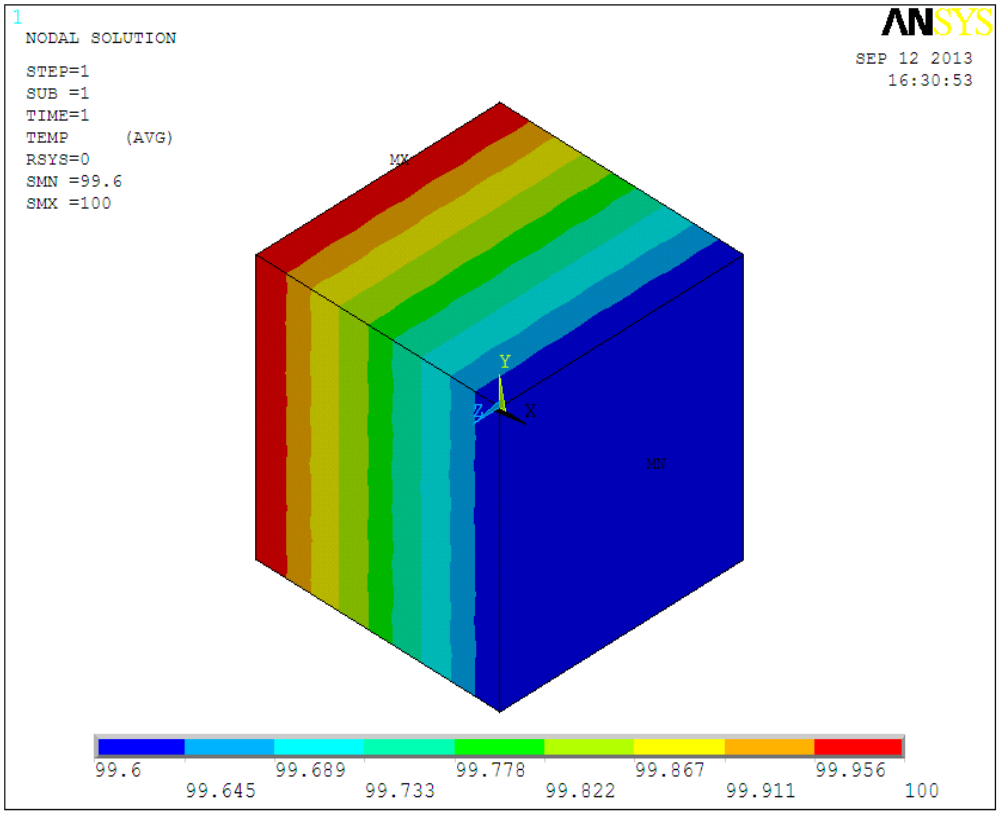

Figure 5.4e Temperature profile obtained for epoxy filled with 9.42 vol % TiO_2

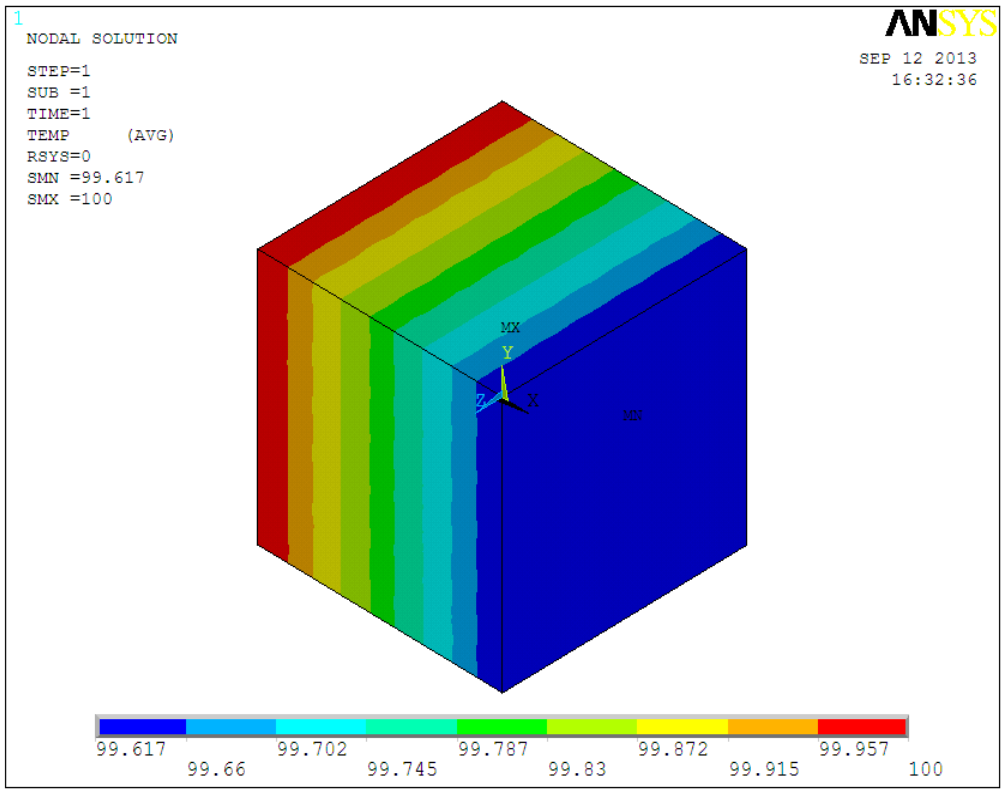

Figure 5.4f Temperature profile obtained for epoxy filled with 11.3 vol % TiO_2

5.2. Effective Thermal Conductivity: Numerical and Experimental Methods

From the temperature profile, the value of effective thermal conductivity of each composite sample is estimated by the basic one dimensional heat conduction equation. As expected the value of k_{eff} comes out to be different for composites with different TiO_2 content. These values obtained from FEM simulation for composites with different filler concentrations ranging from 0 to 11.3vol% are presented in Table 5.1. It also presents the corresponding experimentally measured values of conductivity of the composites having same filler concentrations. Further, the percentage error associated with each FEM simulated value with respect to the measured value is given in this table. The comparison of results obtained from numerical analysis and experimental measurement is illustrated graphically in Figure 5.5.

It is seen from both Table 5.1 and Figure 5.5 that the values of k_{eff} obtained from numerical analysis and experimental effort are in fairly good agreement (with error lying in the range 0 to 2%) up to a filler concentration of 11.3 vol% and that there is an appreciable improvement in thermal conductivity of the composite as the concentration of TiO_2 particle is increased. With incorporation of 11.3 vol% of TiO_2 particle, the conductivity is found to be increased by 21.26% with respect to that of neat epoxy resin.

Table 5.1 Effective thermal conductivities of the composite samples and associated percentage errors

Sample	Filler Content (Volume %)	Effective Thermal Conductivity(W/m-K)		
		FEM	Experimental	Percentage Error
1	0	0.363	0.363	0
2	1.4	0.373	0.3702	0.7
3	3.35	0.388	0.3853	0.7
4	5.23	0.409	0.4011	1.9
5	7.85	0.44	0.4354	1.05
6	9.42	0.455	0.4503	1.04
7	11.3	0.474	0.4702	0.8

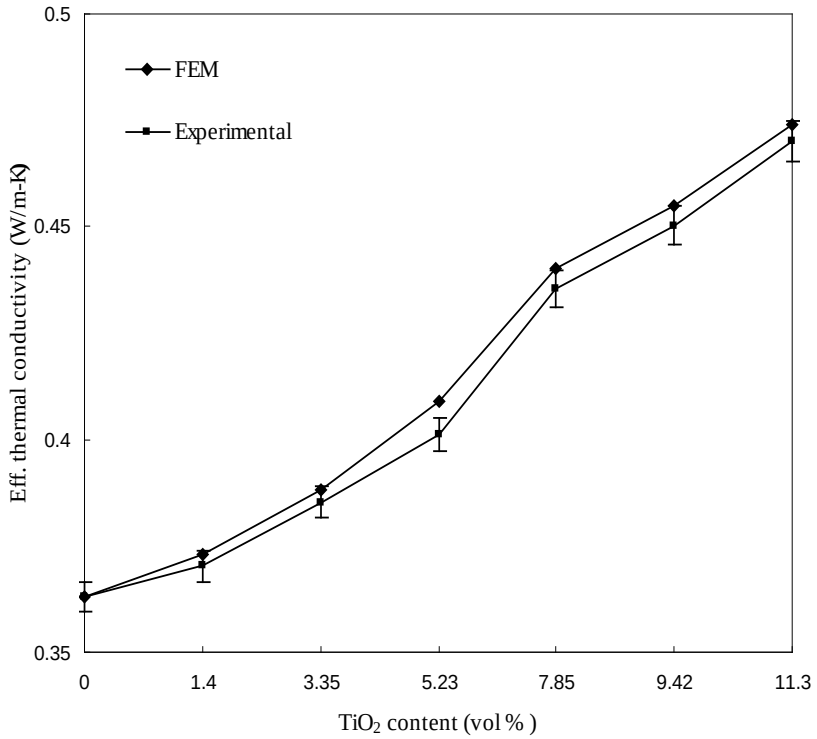

Fig 5.5 Variation of k_{eff} of composites with TiO_2 content (Comparison of FEM and experimental results)

$$k_{eff} = \xi \frac{1}{\frac{1}{k_p} - \frac{1}{k_p}\left(\frac{6\phi_f}{\pi}\right)^{\frac{1}{3}} + \frac{4}{\left(k_p\left(\frac{4\pi}{3\phi_f}\right)^{\frac{2}{3}} + \left(\frac{2\phi_f}{9\pi}\right)^{\frac{1}{3}} 2\pi\left(k_f - k_p\right)\right)}} \quad (11)$$

The correlation given in equation (11) can be used to estimate k_{eff}, by suitably tuning the value of ξ .

From the above correlation (Equation 11), the effective thermal conductivities of the composites under study are estimated for different filler concentrations. In order to validate the correlation and attain a close approximation with experimental results, a suitable correction factor ξ =0.65 for epoxy-TiO_2 composites is chosen. The theoretically estimated k_{eff} values along with the

corresponding experimentally measured values are presented in Table 5.2. The variation of k_{eff} as a function of TiO_2 content is illustrated in Figure 5.10.

Table 5.2 Thermal conductivity values obtained for the composites from different methods

Filler Content	Effective thermal conductivity (W/m-K)	
	Theoretical	Measured
0	0.363	0.363
2.5	0.363	0.364
5.0	0.377	0.398
7.5	0.421	0.431
10.0	0.466	0.483
12.5	0.513	0.531
15.0	0.568	0.585
17.5	0.618	0.669
20.0	0.676	1.108
22.5	0.742	1.151
25.0	0.812	1.173

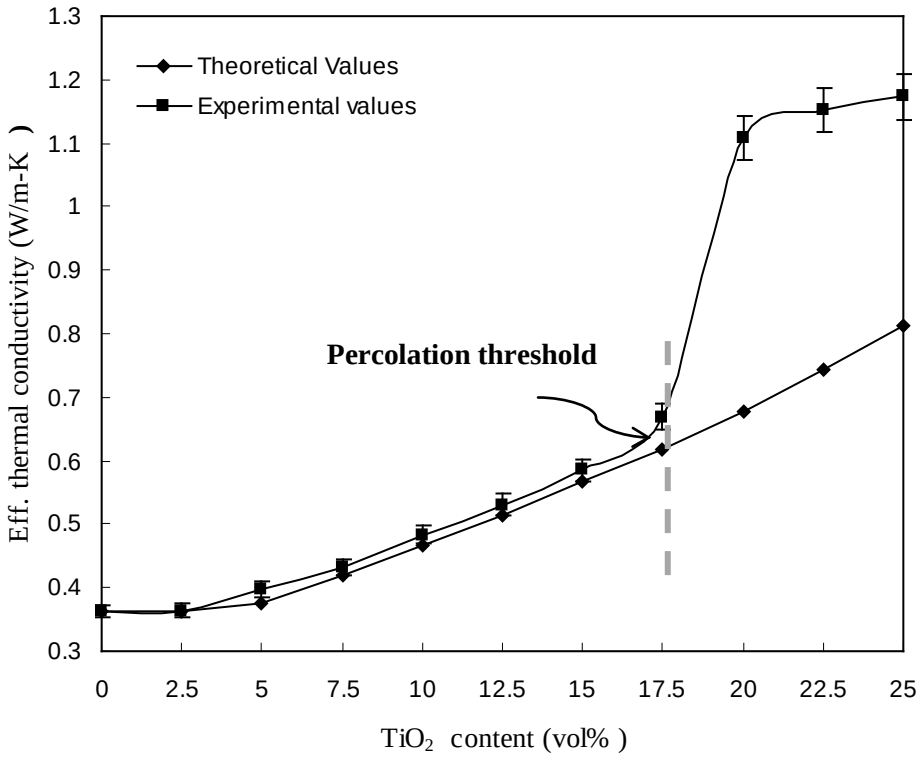

Figure 5.10 Variation of effective thermal conductivity with TiO_2 content (Comparison of Theoretical and Experimental results)

On comparing, it is noted that there is a reasonably good agreement between the theoretical values with the experimental results up to a TiO_2 concentration of 17.5 vol%. But just beyond this, a sudden jump in the measured value of thermal conductivity of the composites is noticed as seen in Figure 5.10. This feature of sudden rise in k_{eff} is not obtained while using the proposed correlation which indicates only a monotonic and almost linear increase in k_{eff} with increase in filler content. It reveals that TiO_2 particulates exhibit a percolation behavior in epoxy resin at a volume fraction of 17.5 %. This stage is called the percolation threshold. It can be observed from Figure 5.10 that below this percolation threshold, enhancement of thermal conductivity is negligible and the threshold conductivity of the composites is almost equal to or slightly higher than that of the matrix polymer. But just after 17.5 vol% of TiO_2 concentration, the unexpected rise occurs. This is the critical concentration at which TiO_2 particles start contacting with each other and hence the actual size of the agglomerates becomes larger. Consequently, the heat conduction performance of epoxy composites incorporating TiO_2 exceeds expectations. With addition of 25 vol% of TiO_2, the thermal conductivity of epoxy composite improves by about 223 %. In filled polymer composites, fillers are connected and conduction networks are formed in the case of high filler content. The fillers are isolated by the matrix in the case of low filler content [135].

Thermal conductivity of the composite is usually the same as that of the polymer as long as the filler concentration is zero or little higher than zero. When the polymer is filled with any conductive filler (having conductivity higher than that of polymer) like TiO_2, the effective conductivity of the composite increases making the polymer more conductive. This trend is observed in case of all the epoxy-TiO_2 composites considered in this study.

5.4. Glass Transition Temperature (T_g)

The glass transition temperatures (T_g) of the composites are measured with a Perkin Elmer DSC-7 thermal mechanical analyzer (TMA). Figure 5.11 shows

the variation of glass transition temperature of the epoxy-TiO_2 composites with different filler loading.

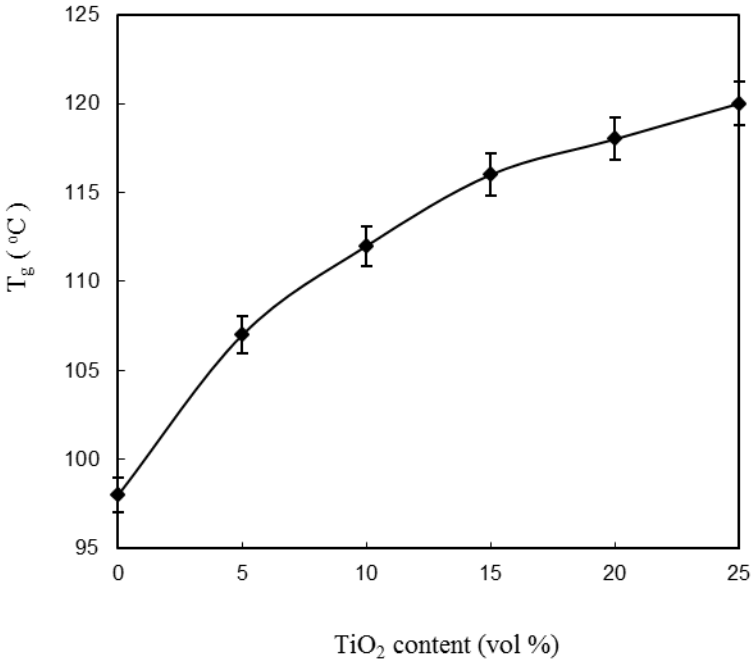

Figure 5.11 Variation of glass transition temperature with TiO_2 content

It is observed that T_g of epoxy increases from 98°C to 120°C with incorporation of 25 vol% of TiO_2. The increase in T_g of the epoxy-TiO_2 composites can be due to the strong interaction between the TiO_2 and epoxy-matrix. The interaction between the filler particles and the polymer restricts the mobility of the polymer chain. Similar observations have also been reported in the past [136, 137].

5.5. Coefficient of Thermal Expansion (CTE)

A low CTE is desirable for applications like micro-electronics encapsulation to maintain the dimensional stability of the material and can be obtained by dispersing fillers with low CTE within the matrix. TiO_2 is known to have low CTE [109], hence it is expected that its addition would reduce considerably this

property of the epoxy matrix. The variation of CTE of epoxy-TiO_2 composites with filler content is shown in Figure 5.12.

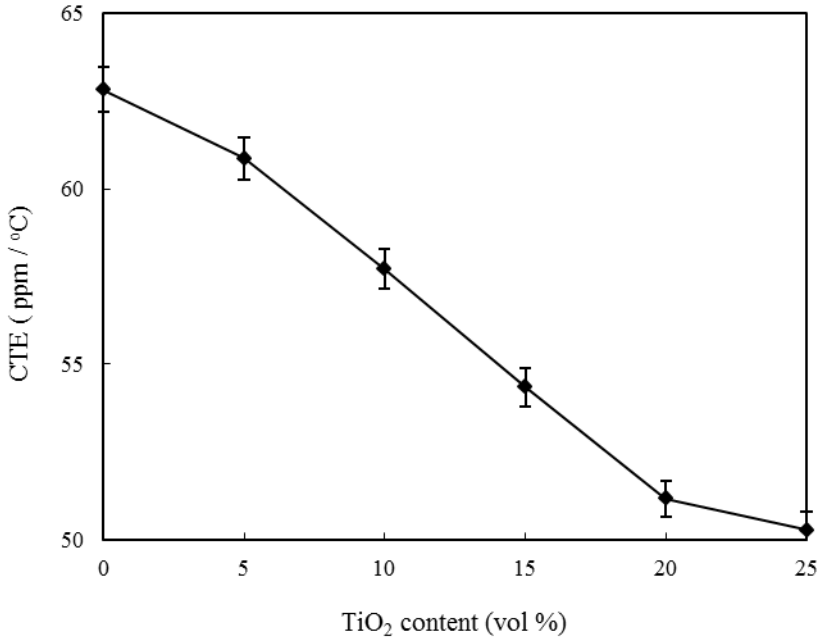

Figure 5.12 Variation of coefficient of thermal expansion with TiO_2 content

It is observed that CTE of neat epoxy which is 62.83 ppm/˚C gradually decreases to 50.28 ppm/˚C with addition of 25 vol % of TiO_2. The low CTE of TiO_2 (about 8.6 ppm/°C) and the constraint of deformation of the epoxy-matrix due to the interaction of TiO_2 and epoxy are responsible for the reduction in CTE of the epoxy–TiO_2 composites. A maximum decrease of 20 % in CTE is observed for 25 vol% loading of TiO_2. This results suggest that CTEs can be tuned by tailoring the amount of TiO_2 added, which may find applications for smart materials and thermal management in electronics applications.

Chapter Summary

This chapter has provided:

- The results of the numerical analysis and experiments conducted to evaluate the thermal conductivity of the polymer composites under study

- The validation of proposed theoretical models through experimental results
- The effect of TiO_2 in improving the heat conduction capability of epoxy.
- A complete picture on the percolation behavior exhibited by the fillers in regard to the conductivity of polymer composites
- Effects of TiO_2 on the modified glass transition temperature and coefficient of thermal expansion of composites

The next chapter presents the thermal characteristics of PP-TiO_2 composites under this research which would enable us to explore possible use of the composites in potential application areas.

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Chapter 6

Results and Discussion – III

THERMAL CHARACTERISTICS OF THE POLYPROPYLENE-TiO_2 COMPOSITES

This chapter presents the test results for various thermal properties such as effective thermal conductivity (k_{eff}), glass transition temperature (T_g) and coefficient of thermal expansion (CTE) of all the PP-TiO_2 composites under this investigation. The validation of the proposed theoretical model in regard to the determination of effective thermal conductivity is presented in this part of the thesis. This chapter also explores the consequence of inter-connectivity among the TiO_2 micro fillers in the PP matrix, leading to higher $k_{eff.}$ The effects of particulate fillers on T_g and CTE of the composites are also discussed.

6.1 EFFECTIVE THERMAL CONDUCTIVITY (k_{eff})

Effective thermal conductivities of polypropylene composites filled with TiO_2 fillers are evaluated theoretically and experimentally. Theoretical values are estimated for composites with different filler concentrations using some of the established empirical models in addition to the model proposed in this work. The interpretation and comparison of results obtained from different methods for are presented.

Table 6.1 presents the measured values of k_{eff} of the TiO_2 filled PP composites with the values determined using some of the already existing theoretical models and correlations like Rule of Mixture (ROM)[117], Maxwell's equation [138] , Lewis and Nielsen's equation [106] and the proposed model.

Table 6.1 Effective thermal conductivities of composites obtained from different models and experiment

Filler Content (Vol%)	Effective Thermal Conductivity (W/m-K)				
	Rule of Mixture	Maxwell's Model	Lewis & Nelson's Model	Proposed Model	Experimental
0	0.111	0.111	0.111	0.110	0.111
2.5	0.112	0.118	0.117	0.112	0.127
5.0	0.115	0.126	0.124	0.131	0.148
7.5	0.118	0.136	0.133	0.149	0.167
10.0	0.122	0.145	0.142	0.167	0.188
12.5	0.125	0.155	0.153	0.186	0.211
15.0	0.130	0.166	0.164	0.207	0.230
17.5	0.133	0.177	0.177	0.229	0.369
20.0	0.137	0.189	0.193	0.254	0.394
22.5	0.141	0.202	0.210	0.282	0.401
25.0	0.146	0.216	0.231	0.315	0.407

Figure 6.1 presents a comparison of k_{eff} values obtained from various existing models and the proposed correlation (Eq.5.9) with the corresponding experimentally measured values for the composites with different TiO_2 concentrations. It is seen that with increase in the volume fraction of TiO_2 micro-particles, the effective thermal conductivity of polypropylene composite improves irrespective of the method or model used for the purpose. It is further noted that the theoretical values are always less than the corresponding measured values for composites of any compositions. While different models and correlations yield different values for the effective conductivity, the results obtained from the proposed model are in close approximation with the experimentally measured values for a certain range of filler concentration. The comparison curves in Figure 6.1 thus indicate the validation of the proposed

model with a correction factor of 0.69 for polypropylene-TiO_2 composites up to a filler concentration of about 15%.

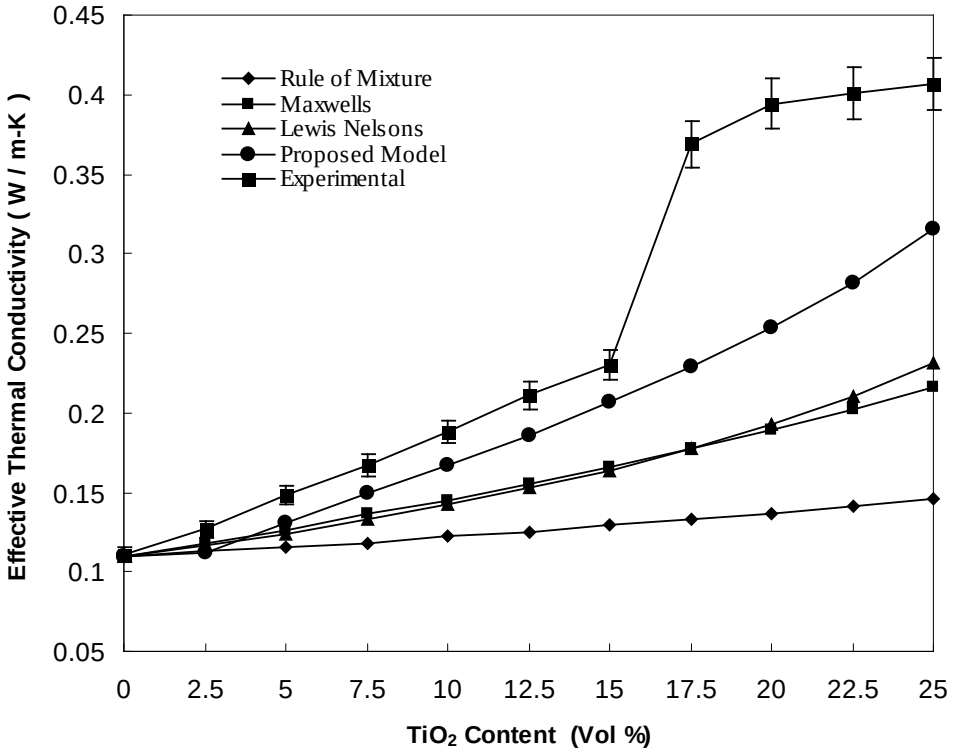

Figure 6.1 Comparison of k_{eff} values obtained from various methods

When the polymer is filled with any conductive filler (having conductivity higher than that of polymer) like TiO_2, the effective conductivity of the composite increases making it more conductive. This trend is observed in case of all the PP-TiO_2 composites considered in this study. It is found that with increase in the TiO_2 content, the value of k_{eff} increases and an increment as high as 266 % is recorded for PP filled with 25 vol % of the micro fillers. Initially, at low filler concentration, since the number of the conductive particles is insufficient to form a continuous conducting path, the conductive domains are insulated from each other by the polymer medium and the heat conducting behavior observed is not remarkable. As the filler (TiO_2) volume increases, the conductive particles appear to contact each other forming a continuous network for the transfer of heat. In the present work, at a volume fraction of 15 vol%, the TiO_2 particles show percolation behavior in polypropylene matrix and at this filler

concentration, the value of thermal conductivity increases suddenly. Figure 6.2 presents a comparison of k_{eff} values given by the proposed correlation with the experimentally measured one for different compositions. This figure indicates the percolation threshold in regard to thermal conduction in the PP-TiO_2 composite system.

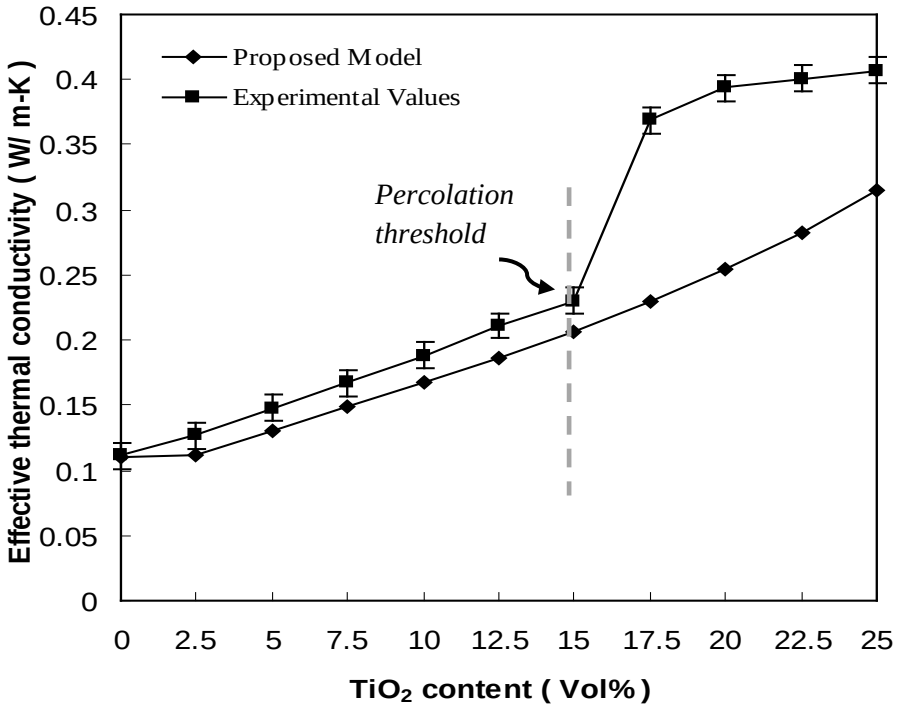

Figure 6.2 Variation of effective thermal conductivity with TiO_2 content (Comparison of theoretical and experimental results)

The percolation threshold point is the point at which a network first spans the system. This is the first appearance of long-range connectivity**.** According to experimental findings, as already mentioned, the effective thermal conductivity increases rapidly when the filler volume fraction exceeds the percolation threshold. Furthermore, the effective thermal conductivity increases non-linearly with the increase in filler content due to the gradual development of density of the network. The precise location of the percolation threshold is affected by many factors, including the size, aspect ratio and distributions of the conductive particles within the matrix body [135,139,140]. Immediately after the percolation threshold, even a slight increase in the concentration of conductive TiO_2 particles are found to greatly increase in the conducting network leading to

a substantial improvement in effective thermal conductivity of the composites. Percolation theory deals with the effects of varying the connectivity of elements (e.g, particles, sites, or bonds) on a random system. According to experimentally determined k_{eff} of the composites, the effective thermal conductivity of the composites increases rapidly after the filler volume fraction reaches the percolation threshold. Furthermore, the effective thermal conductivity increases non-linearly with the increase in filler content due to the gradual development of density of the network as already mentioned.

The experimental findings further reveal that the effective thermal conductivity of the PP-TiO_2 composites is always higher than that of neat polypropylene. Composite with fixed TiO_2 content of 25 vol%, the k_{eff} is about 0.407 W/m-K. This enhancement in k_{eff} is about 3.5 times than that of the neat polypropylene (0.11 W/m-K).

6.2. Glass Transition Temperature (T_g)

The glass transition temperature (T_g) of the composites are measured with a Perkin Elmer DSC-7 thermal mechanical analyzer (TMA). Figure 6.3 shows the variation of glass transition temperature of the PP-TiO_2 composites with different filler loading. It is observed that T_g of PP increases from -14.94°C to 9.04°C with incorporation of 25 vol% of TiO_2. The increase in T_g of the PP-TiO_2 composites can be due to the strong interaction between the TiO_2 and PP-matrix. The interaction between the filler particles and the polymer restricts the mobility of the polymer chain. Similar observation of improved T_g with ceramic fillers has also been reported by previous investigators [136, 137].

6.3. Coefficient of Thermal Expansion (CTE)

As components in electronic devices suffer from temperature fluctuations during operation, a low CTE is desirable for the materials used in such applications to maintain the dimensional stability. For polymeric material, this can be obtained by dispersing fillers with low CTE within the matrix. TiO_2 is known to have low CTE [109], hence it is expected that its addition would reduce the CTE of the PP matrix. Variation of CTE of PP-TiO_2 composites with filler content is shown in Figure 6.4.

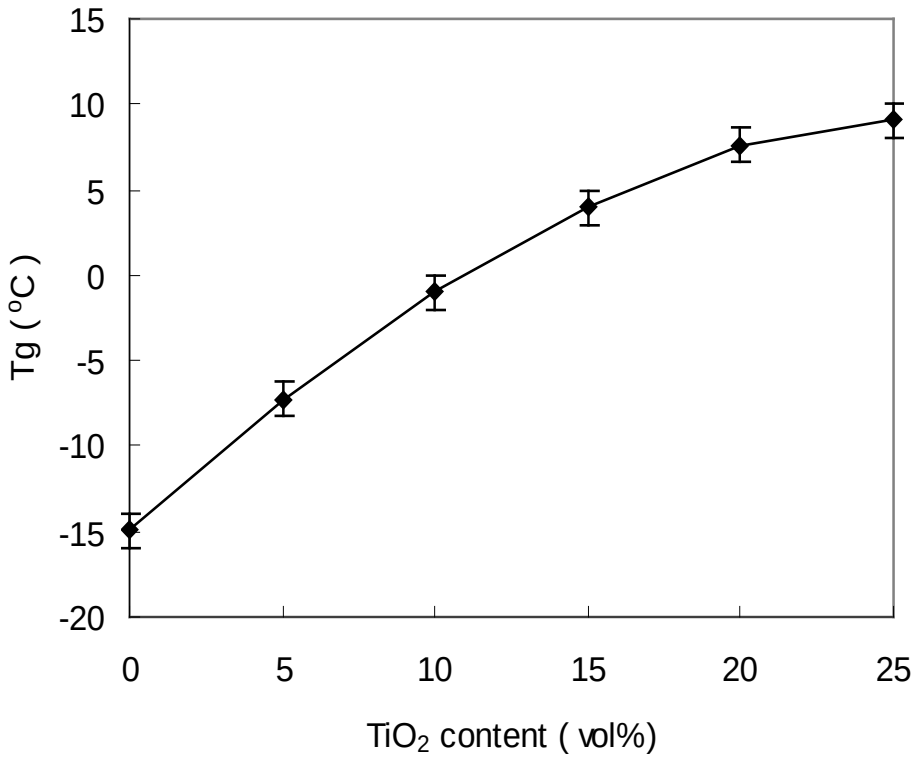

Figure 6.3 Variation of glass transition temperature with TiO_2 content

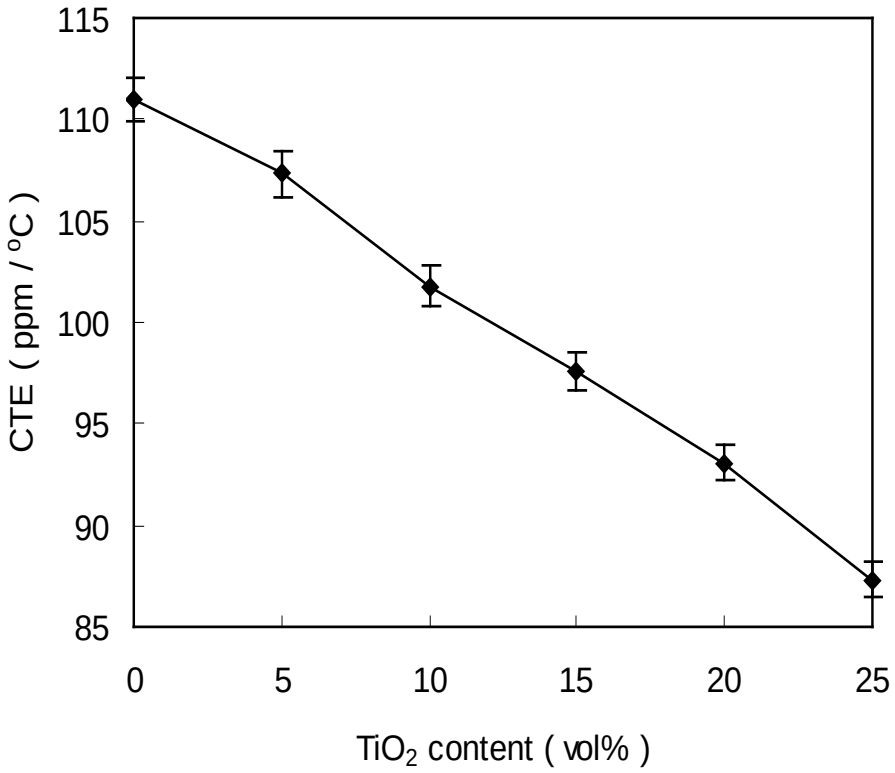

Figure 6.4 Variation of coefficient of thermal expansion with TiO_2 content

It is observed that CTE of neat polypropylene which is 111 ppm/˚C gradually decreases to 87.3 ppm/˚C with addition of 25 vol % of TiO_2. The low CTE of TiO_2 (about 8.6 ppm/°C) and the constraint of deformation of the PP-matrix due to the interaction of TiO_2 and PP are responsible for the reduction in CTE of the PP-TiO_2 composites. A maximum reduction of 21.35 % in CTE is observed for 25 vol% loading of TiO_2. This results suggest that CTEs can be tailored by tuning the amount of TiO_2 added, which may find applications for thermal management in electronic applications.

Chapter Summary

This chapter has provided:

- The test results to evaluate the thermal conductivity of the PP-TiO_2 composites and the validation of the proposed theoretical model through experimental results.
- The effects of TiO_2 content in improving the heat conduction capability of polypropylene.
- A complete picture on the percolation behavior exhibited by the fillers in regard to the conductivity of polymer composites
- Effects of TiO_2 on the modified glass transition temperature and coefficient of thermal expansion of composites

The next chapter provides the summary of the research findings outlines specific conclusions drawn and suggests ideas and directions for future research.

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Chapter 7

SUMMARY AND CONCLUSIONS

The research reported in this thesis broadly consists of three parts:

- The first part has provided the description of the materials used and the details of the experiments that are done during this research. It also presents the test results in regard to the physical, mechanical and micro-structural characteristics of the epoxy and polypropylene composites filled with micro-sized TiO_2 particles.
- The second part is about the development of a theoretical heat conduction model based on which a mathematical correlation has been proposed for estimation of effective thermal conductivity of polymer composites with uniformly distributed micro-sized particulate fillers. In this part, the correlation is validated for TiO_2 filled polymers through numerical analysis and experimentation.
- The last part has reported on the epoxy and polypropylene composites in regard to their other thermal characteristics such as glass transition temperature (T_g) and coefficient of thermal expansion (CTE). The effects of TiO_2 content on these properties of epoxy and polypropylene have been studied experimentally.

7.1 Summary of Research Findings

The performance of any new composite product is often judged by its response under different physical, mechanical and thermal conditions as it becomes essential for selecting the material of proper composition for any given application. Therefore, in the present work, a wealth of property data has been

generated for a series of epoxy-TiO_2 and polypropylene-TiO_2 composites by fabricating them in the laboratory and by conducting various physical, mechanical and thermal tests on them under controlled laboratory conditions. It is found that by incorporating micro-sized TiO_2 particulates into these polymers, its effects, as expected are achieved in the form of modified physical, mechanical and thermal properties. Due to the presence of TiO_2 micro-fillers, changes in their heat conduction behavior are seen. When TiO_2 is added to in epoxy and polypropylene matrices, the effective thermal conductivity of the composites is ameliorated as TiO_2 is conductive in nature. Thermal bridges are formed within the matrix body at and beyond a stage called percolation threshold resulting in a rise in conductivity. It is seen that there is a sudden jump in the composite thermal conductivity at this point of filler concentration. Effects of TiO_2 on the glass transition temperature and coefficient of thermal expansion of the composites are also found to be substantial.

7.2 Conclusions

This analytical and experimental investigation on epoxy and polypropylene composites filled with TiO_2 micro-particles has led to the following specific conclusions:

1. Successful fabrication of particulate filled epoxy-TiO_2 composites by hand layup technique and polypropylene-TiO_2 composites by compression moulding route is possible.

2. Incorporation of TiO_2 particles as filler modifies the tensile and compressive strengths of the composites. It is noticed that with addition of TiO_2 particles, tensile strength of both the composites is marginally decreased and this decrement is a function of the filler content. The micro-hardness, density and porosity of these composites are also greatly influenced by the filler content.

3. A theoretical correlation to estimate the effective thermal conductivity of particulate filled composites is proposed based on the one dimensional heat conduction model. It is seen that this serves as a good empirical model for spherical inclusions and that the proposed correlation can therefore very well be used to estimate k_{eff} for composites within the percolation limit.

4. It is propitious that the incorporation of TiO_2 particles results in significant improvement in the thermal conduction capability of both epoxy as well as polypropylene resin. It is found that with increase in the TiO_2 content up to 25 vol%, the value of effective thermal conductivity (k_{eff}) improves by 223% for epoxy and 266% for polypropylene based composites.

5. With increasing TiO_2 content in the composite, the value of k_{eff} keeps on increasing. It is seen that the results obtained from the proposed correlation are in good agreement with experimental results up to a filler concentration of about 17.5 vol % for epoxy and 15 vol% for polypropylene composite. The TiO_2 particles thus show percolation behaviour at these volume fractions (17.5% for epoxy and 15% for PP) at which a sudden jump in the thermal conductivity is noticed. This is the critical concentration, called the percolation threshold, at which TiO_2 particles start contacting with each other within the respective polymer resin and hence the actual size of the agglomerates becomes larger.

6. It is observed that the T_g of epoxy (98^0C) gradually increases to 120 °C as the TiO_2 content increases from 0 to 25vol%. The increase in T_g can be attributed to strong interaction between the filler and the epoxy-matrix which restricts the mobility of the polymer chain. Similarly, T_g of PP-TiO_2 composites also gradually increases from -14.94 ^{0}C to about 9.04 ^{0}C as the TiO_2 content in PP increases from 0 to 25vol%.

7. It shows that the CTE of the composite decreases with the increase in TiO_2 content. Low CTE of TiO_2 (about 8.6 ppm/^{0}C) and the constraint of deformation of the epoxy-matrix due to the interaction of TiO_2 and epoxy are responsible for the reduced CTE of the composites. Incorporation of TiO_2 in PP too substantially reduces the CTE of PP-TiO_2 composites.

7.3 Scope for Future Research

The present research work leaves a wide scope for future investigators to explore many other aspects of such particulate filled composites. Some recommendations for future research include:

- Possible use of ceramic fillers other than TiO_2 and polymeric resins other than epoxy and polypropylene in the development of new composites.
- Exploring the possibility of using natural fibers along with ceramic particulates to fabricate such composites with improved functional properties.
- Cost analysis of these composites to assess their economic viability in industrial applications.

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Appendix- A1

List of publications from this research work

International Journals

1. **Madhusmita Sahu** and Alok Satapathy**,** "A Study on Micro-sized Titanium Oxide Filled Epoxy with Enhanced Heat Conductivity for Microelectronic Applications", **Particulate Science and Technology, DOI:** 10.1080/02726351.2014.941081.
2. **Madhusmita Sahu** and Alok Satapathy, "A Study on enhancement of thermal properties of TiO_2 filled Polymer Composites", Accepted for publication in **Procedia Engineering.**
3. **Madhusmita Sahu** and Alok Satapathy**,** "Thermal Conductivity of TiO_2 Filled Epoxy Composites: A Numerical and Experimental Investigation." Communicated to **Journal of Composites.**

International Conferences

1. **Madhusmita Sahu** and Alok Satapathy**,** "A Study on Effective Thermal Conductivity of TiO_2-Epoxy Composites." International Conference on Advancement in Polymeric Materials (APM 2013): Lucknow, Feb 2013.
2. **Madhusmita Sahu** and Alok Satapathy**,** "A Study on Titanium Oxide Micro-Particles Filled Epoxy with Enhanced Heat Conductivity for Microelectronic Packaging Applications." International Conference on Powder Granule and Bulk Solids: Innovations and Applications ***PGBSI-2013,*** Nov 2013***, Thapar Univrsity, Patiala.***
3. **Madhusmita Sahu** and Alok Satapathy**,** "Enhanced Thermal Properties of TiO_2 Filled Thermoplastic Composites." (Accepted) for International Conference on Advancement in Polymeric Materials (APM 2014): Bhubaneswar, Feb 2014

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Appendix- A2

Brief Bio-data of the Author

The author, Madhusmita Sahu, born on 27-05-1985 graduated in Mechanical Engineering from Biju Patnaik University of Technology (BPUT) in the year 2007. Before joining for the M.Tech.(Research) programme at the National Institute of Technology, Rourkela, she had served as a faculty in the Department of Mechanical Engineering at IEC College of Engineering and Technology, Greater Noida and then as a Junior Research Fellow in a DST sponsored project on *Bulk Utilization of Fly Ash*. She has authored 02 research papers in international journals and has 03 papers in various international conferences to her credit. In the postgraduate programme, she has worked in the area of study on the thermal characteristics of particulate filled polymer composites.

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